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Report No. 8

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REPORT

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THE OHIO STATE UNIVERSITY
RESEARCH FOUNDATION

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INVESTIGATION OF: Research in Nitromonomers and Their Application to Solid Smokeless Propellants

SUBJECT OF REPORT: Status Report for the Period Feb. 1, 1952 to August 15, 1952

SUBMITTED BY: L. Zeldin, L. Friedman, D. Ley, E. Roberson, D. Brain, T. Moritsugu and H. Shechter

DATE: August 15, 1952

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ABSTRACT

1. Reaction of 1,1,1-trinitroethane and n-butyllithium in benzene for three hours at 0° occurs very slowly by oxidation-reduction to give lithium 1,1-dinitroethane in 17.0% conversion; 1,1,1-trinitroethane was recovered in 38% yield.

2. Reaction of 1,1,1-trinitroethane and potassium ethoxide in the presence of benzyl cyanide results in formation of potassium ethyl 2,2-dinitroethyl ether in 89.6% yield. There was no evidence for elimination-addition involving benzyl cyanide anion to give potassium 3-cyano-1,1-dinitro-3-phenylpropane.

3. An improved procedure has been developed for preparation of pure 2,2-dinitroethylguanidine (77.7% yield) from 1,1,1-trinitroethane and guanidine in ethanol at 0-5°. The other products of reaction have been tentatively identified as guanidine hydronitrite (the major component) and nitrosoguanidine. A quantitative analytical procedure for determining the composition of 2,2-dinitroethylguanidine in the reaction product has been developed based on the ultra-violet absorption characteristics of pure 2,2-dinitroethylguanidine in ethanol.

4. The x-ray crystallographic properties of N-(2,2-dinitroethyl)-piperidine prepared by reaction of either (1) piperidine and 1,1,1-trinitroethane, (2) piperidine and trimethylammonium N-(2-nitroethyl-2-nitronate), or (3) piperidine and 2,2-dinitroethylguanidine have been determined. As a result of this study it is believed that the structures assigned to the products obtained from reaction of 1,1,1-trinitroethane with piperidine, trimethylamine, and guanidine are correct.

5. Reaction of piperidine and 1-bromo-1,1-dinitroethane results in oxidation-reduction to give piperidinium 1,1-dinitroethane (78% yield); the other products of reaction have not been identified as yet. Piperidinium 1,1-dinitroethane was also prepared by reaction of piperidine and 1,1-dinitroethane (89%).

6. Reaction of methyl iodide and silver 1,1-dinitroethane in anhydrous acetonitrile at 0-5° results in formation of 2,2-dinitropropane (13.7%), 1,1-dinitroethane (9.8%), formaldehyde, and a series of unidentified products.

7. Convenient laboratory procedures have been developed for preparation of sodium and lithium trimethoxyborohydrides by reaction of sodium or lithium hydride and trimethylborate in tetrahydrofuran. Selective reductions of aliphatic nitroaldehydes, ketones, and esters with sodium trimethoxyborohydride yield the corresponding nitrocarbinols.

Reduction of 4-methyl-4-nitro-1-pentanal and 5,5-dinitro-2-hexanone with sodium trimethoxyborohydride gave 4-methyl-4-nitro-1-pentanol (90%) and 5,5-dinitro-2-hexanol (89%); reactions of methyl 4-methyl-4-nitropentanoate and methyl 4-nitrobutanoate with sodium trimethoxyborohydride in refluxing tetrahydrofuran yield 4-methyl-4-nitro-1-butanol (92%) and 4-nitro-1-butanol (80%).

Selective reduction of nitro acid chlorides with sodium trimethoxyborohydride results in formation of nitroaldehydes. Reduction of p-nitrobenzoyl chloride, 4-methyl-4-nitropentanoyl chloride, 4,4-dinitropentanoyl chloride, 4-nitropentanoyl chloride, and 4-nitrobutanoyl chloride with sodium trimethoxyborohydride gave p-nitrobenzaldehyde (74%), 4-methyl-4-nitropentanal (66%), 4,4-dinitropentanal (72%), 4-nitropentanal (63%), and 4-nitrobutanal (36%), respectively.

8. 2-Methyl-1-nitropropene may be reduced to 2-methyl-1-nitropropane by reaction with sodium trimethoxyborohydride or with lithium borohydride in 63.4% and 48.4% yields, respectively. Selective reaction of 2-nitro-2-butyl acetate with lithium borohydride or sodium trimethoxyborohydride yields 2-nitro-1-butanol and ethanol; no 2-methyl-1-nitropropane was obtained from these reactions.

9. 2-Methyl-1-nitropropane (70%), 1-nitropentane (39%), 3-methyl-1-nitrobutane (61%) and 3,3-dimethyl-1-nitrobutane (23%) were prepared by reaction of silver nitrite with 1-iodo-2-methylpropane, 1-bromopentane, 1-bromo-3-methylbutane and 1-bromo-3,3-dimethylbutane, respectively. Oxidative-nitration of 2-methyl-1-nitropropane, 1-nitropentane, 3-methyl-1-nitrobutane, 3,3-dimethyl-1-nitrobutane, and cyclohexylnitromethane gave 1,1-dinitro-2-methylpropane (55%), 1,1-dinitropentane (75%), 1,1-dinitro-3-methylbutane (61%), 3,3-dimethyl-3,3-dinitrobutane (43%), and cyclohexyldinitromethane (65%).

10. The ionization constants of a series of 1,1-dinitroalkanes have been determined with improved techniques at 25 $\pm$ 0.1°C in 17.8 $\pm$ 0.1% methanol-water and 44.25 $\pm$ 0.15% methanol-water. The ionization data obtained in the two solvent systems are: 1,1-dinitropropane, K_a $2.2 \pm 0.2 \times 10^{-6}$, K_a $6.2 \pm 0.1 \times 10^{-7}$; 1,1-dinitrobutane, K_a $3.5 \pm 0.05 \times 10^{-6}$, K_a $1.2 \pm 0.05 \times 10^{-6}$; 1,1-dinitropentane, K_a $3.0 \pm 0.05 \times 10^{-6}$, K_a $1.2 \pm 0.1 \times 10^{-6}$; 1,1-dinitro-2-methylpropane, K_a $1.2 \pm 0.1 \times 10^{-7}$, K_a $3.8 \pm 0.2 \times 10^{-8}$; 2,2-dimethyl-1,1-dinitropropane, K_a $5.6 \pm 0.05 \times 10^{-9}$, K_a 1.7×10^{-9}; 1,1-dinitro-3-methylbutane, K_a $2.1 \pm 0.1 \times 10^{-6}$, K_a $8.9 \pm 0.05 \times 10^{-7}$; phenyldinitromethane, K_a $4.8 \pm 0.2 \times 10^{-5}$, K_a 1.6×10^{-5}; cyclohexyldinitromethane, K_a $4.5 \pm 0.1 \times 10^{-8}$, K_a $4.1 \pm 0.1 \times 10^{-8}$ and 3,3-dimethyl-1,1-dinitrobutane, K_a (44.25% MeOH) $2.8 \pm 0.05 \times 10^{-6}$.

The ultra-violet absorption spectra and the solubilities in water of the potassium salts of 1,1-dinitropentane, 1,1-dimethyl-3-nitrobutane, 3,3-dimethyl-1,1-dinitrobutane, and cyclohexyldinitromethane have been determined. The effect of the dielectric constants of methanol-water mixtures on the ionization constants of phenyldinitromethane has been studied.

11. Reaction of 2-nitropropane and methyl propiolate at 0-25° in the presence of sodium methoxide occurs readily to give methyl 4-methyl-4-nitro-2-pentenoate in 55.4% yield. Addition of 1,1-dinitroethane to methyl propiolate catalyzed by benzyltrimethylammonium hydroxide yields methyl 4,4-dinitro-2-pentenoate (tentative); identification of this unstable product is in progress.

TABLE OF CONTENTS

TABLE OF CONTENTS (Cont'd.)

TABLE OF CONTENTS (Cont'd.)

Page

EXPERIMENTAL (Cont'd.)

TABLE OF CONTENTS (Cont'd.)

1. **REACTIONS OF 1,1,1-TRINITROETHANE WITH n-BUTYL LITHIUM, BENZYLCYANIDE-POTASSIUM ETHOXIDE, AND GUANIDINE; LITHIUM 1,1-DINITROETHANE, POTASSIUM ETHYL 2,2-DINITROETHYL ETHER, AND 2,2-DINITROETHYLGUANIDINE.**

The reactions of various bases with 1,1,1-trinitroethane[1] have been subject to continued investigation in these laboratories. The bases which have been investigated are: potassium diethylmalonate, potassium malononitrile, potassium acetylacetone, potassium 2-propanenitronate, trimethylamine, piperidine, potassium n-butylmercaptan, guanidine, phenyl magnesium bromide, potassium cyanide, and n-butyl lithium. The emphasis in this research is toward developing a synthesis of 1,1-dinitroethylene or a general reaction leading to carbon-alkylated products in accord with the following schematic equation (Equation 1):

$$2\ (R_1)(R_2)(R_3)C^- + CH_3C(NO_2)_3 \longrightarrow R_2-\overset{R_1}{\underset{R_3}{C}}-CH_2-\overset{NO_2}{\underset{NO_2}{C}}{}^- + NO_2^- + (R_1)(R_2)(R_2)CH \qquad (1)$$

(a) <u>n-Butyllithium:</u> In a previous research period[2] the reaction of n-butyllithium with 1,1,1-trinitroethane was attempted in an effort to synthesize 1,1-dinitrohexane. The reaction took an alternate course and reduction of 1,1,1-trinitroethane to lithium 1,1-dinitroethane occurred; the other products of reaction were not determined. Since the reaction was carried out in anhydrous ethyl ether, it is possible that (1) the solvent plays an important role in determining whether reaction occurs by oxidation-reduction or by elimination-addition and (2) lithium hydroxide (formed by reaction of lithium shot with residual solvent or atmospheric moisture) and lithium bromide present in the ether solution may influence the course of reaction. To minimize the effects of these variables, the reaction of 1,1,1-trinitroethane and n-butyllithium was conducted in benzene solution. It was observed that the reaction is slower than that in ethyl ether solution, but the reaction course is the same in that oxidation-reduction occurs (Equation 2). After three hours reaction time, the yield of lithium 1,1-dinitroethane was only 17.0%; 38.6% of 1,1,1-trinitroethane was recovered. No further work on this system is contemplated at present.

$$CH_3-CH_2-CH_2-CH_2Li + CH_3-C(NO_2)_3 \longrightarrow CH_3-C(NO_2)_2Li + [CH_3-CH_2-CH_2-CH_2(ONO)] \qquad (2)$$

(b) Benzyl Cyanide-Potassium Ethoxide: Reaction of the benzyl cyanide anion and 1,1,1-trinitroethane has been investigated as a possible method of synthesis of substituted 1,1-dinitroalkanes (Equation 3).

$$2C_6H_5\text{-}\bar{C}H\text{-}CN + CH_3\text{-}C(NO_2)_3 \longrightarrow C_6H_5\text{-}CH(CN)\text{-}CH_2\text{-}C(NO_2)_2^- + NO_2^- + C_6H_5\text{-}CH_2CN \quad (3)$$

Benzyl cyanide is an acid of strength comparable to diethyl malonate and may offer the advantage that the anion exists primarily with the negative charge on carbon. Similarly, base-catalyzed alkylation reactions have been frequently reported for benzyl cyanide.[3]

The reaction of benzyl cyanide with 1,1,1-trinitroethane was investigated in the presence of potassium ethoxide. From the literature information of the pK_A values of benzyl cyanide and ethanol and from the reactions of benzyl cyanide in the presence of alkali-metal alkoxides, it can be predicted that the equilibrium position of ethoxide ion and benzyl cyanide will be in favor of the benzyl cyanide anion (Equation 4).

$$C_6H_5\text{-}\bar{C}HCN + C_2H_5OH \rightleftharpoons C_6H_5\text{-}CH_2\text{-}CN + C_2H_5O^- \quad (4)$$

It was found, however, that the reaction product from 1,1,1-trinitroethane, benzylcyanide, and potassium ethoxide was potassium ethyl 2,2-dinitroethyl ether in 89.6 per cent yield (Equation 5), obtained by elimination-addition action of the ethoxide ion on 1,1,1-trinitroethane.[4]

$$2C_2H_5OK + CH_3\text{-}C(NO_2)_3 \longrightarrow C_2H_5\text{-}O\text{-}CH_2\text{-}C(NO_2)_2K + KNO_2 + C_2H_5OH \quad (5)$$

Potassium ethyl 2,2-dinitroethyl ether was identified by ultra-violet and quantitative analyses and by conversion to ethyl 2,2-dinitroethyl ether. It may thus be concluded that elimination-addition reactions of 1,1,1-trinitroethane with ethoxide ion occur much more rapidly than those with benzyl cyanide anion. The reactions of 1,1,1-trinitroethane with potassium benzyl cyanide in tert-butyl alcohol are now being investigated.

(c) Guanidine: It has been previously reported[1] that reaction of guanidine (excess, > two equivalents) and trinitroethane in ethanol results in elimination-addition to give 2,2-dinitroethylguanidine (Equations 6, 7, and 8).

$$H_2N\text{-}\overset{NH}{\overset{\|}{C}}\text{-}NH_2 + CH_3\text{-}C(NO_2)_3 \longrightarrow H_2N\text{-}\overset{NH}{\overset{\|}{C}}\text{-}\overset{+}{N}H_3\overset{-}{NO_2} + [CH_2{=}C(NO_2)_2] \quad (6)$$

$$[CH_2{=}C(NO_2)_2] + H_2N\text{-}\overset{NH}{\overset{\|}{C}}\text{-}NH_2 \longrightarrow H_2N\text{-}\overset{NH}{\overset{\|}{C}}\text{-}NH\text{-}CH_2\text{-}CH(NO_2)_2 \quad (7)$$

$$H_2N\text{-}\overset{NH}{\overset{\|}{C}}\text{-}NH\text{-}CH_2\text{-}CH(NO_2)_2 \rightleftarrows H_2N\text{-}\overset{NH}{\overset{\|}{C}}\text{-}\overset{+}{N}H_2\text{-}CH_2\text{-}C(NO_2)_2^- \quad (8)$$

A much improved procedure is now reported for obtaining pure 2,2-dinitroethylguanidine (77.7% yield) by reaction of guanidine and 1,1,1-trinitroethane in ethanol at 0-5°. A convenient analytical procedure for determining the concentration of 2,2-dinitroethylguanidine in the reaction product has been developed based on the ultra-violet absorption characteristics of pure 2,2-dinitroethylguanidine in ethanol; over the range of concentrations studied, the system 2,2-dinitroethylguanidine-ethanol obeys Beer's law.

The products of reaction of 1,1,1-trinitroethane and guanidine, other than 2,2-dinitroethylguanidine, are believed to be guanidinium nitrite (the major component) and nitrosoguanidine (tentative). Efforts to free guanidinium nitrite from nitrosoguanidine have not been completely successful; the guanidinium nitrite obtained still contained trace contaminants. An analytical procedure for identifying and determining the composition of a mixture of guanidinium nitrite and nitrosoguanidine, based on optical absorption properties, is now being developed.

2. X-RAY CRYSTALLOGRAPHIC PROPERTIES OF 2,2-DINITROETHYLGUANIDINE AND N-(2,2-DINITROETHYL)-PIPERIDINE.

Reactions of 1,1,1-trinitroethane with piperidine, trimethylamine, and guanidine result in formation of N-(2,2-dinitroethyl)-piperidine, trimethylammonium-N-(2-nitroethyl-2-nitronate) and 2,2-dinitroethylguanidine respectively.[1] The structures of trimethylammonium-N-(2-nitroethyl-2-nitronate) and 2,2-dinitroethylguanidine were demonstrated upon determining that these products undergo exchange with piperidine to give N-(2,2-dinitroethyl)-piperidine. The proofs of structures, although definitive, have suffered in that N-(2,2-dinitroethyl)-piperidine, a salt-like product, does not melt sharply (slight decomposition) and thus comparison of melting points and mixed melting points of various samples of N-(2,2-dinitroethyl)-piperidine are not completely satisfactory.

In order to compare samples of N-(2,2-dinitroethyl)-piperidine conclusively, a study of the x-ray powder diffraction characteristics of these materials has been made (See Experimental). As a result of this investigation it may be concluded without question that the structures assigned to the products obtained from reaction of 1,1,1-trinitroethane with piperidine, trimethylamine, and guanidine are correct.

3. REACTIONS OF PIPERIDINE AND 1-BROMO-1,1-DINITROETHANE.

The reactions of various bases with 1-bromo-1,1-dinitroethane are being investigated as methods for the preparation of 1,1-dinitroethylene or its addition products, beta-substituted 1,1-dinitroethanes. 1-Bromo-1,1-dinitroethane is both electrically and sterically similar to 1,1,1-trinitroethane; thus, it is to be expected that these strained polynitroalkanes should exhibit similar behaviors toward various bases. The action of bases with 1-bromo-1,1-dinitroethane would be expected to occur by (1) oxidation-reduction resulting in bimolecular displacement of the bromonium ion (rather than the nitronium ion) (Equation 9) or (2) by elimination-addition resulting in elimination of hydrogen bromide and formation of 1,1-dinitroethylene or its corresponding adducts (Equations 10, 11 and 12). In other investigations[5] it has been reported that bases such as hydroxide or bicarbonate ions

$$R^- + BrC(NO_2)_2\text{-}CH_3 \longrightarrow RBr + {}^-(O_2N)_2C\text{-}CH_3 \qquad (9)$$

$$R^- + CH_3\text{-}C(NO_2)_2Br \longrightarrow R\text{-}H + {}^-CH_2\text{-}C(NO_2)_2Br \qquad (10)$$

$${}^-CH_2\text{-}C(NO_2)_2Br \longrightarrow [CH_2{=}C(NO_2)_2] + Br^- \qquad (11)$$

$$[CH_2{=}C(NO_2)_2] + R^- \longrightarrow R\text{-}CH_2\text{-}C(NO_2)_2^- \qquad (12)$$

or reducing agents such as iodide ion effect oxidation-reduction of 1-bromo-1,1-dinitroethane with formation of salts of 1,1-dinitroethane (as in Equation 9).

In the present study, an investigation is being made of the reactions of piperidine and 1-bromo-1,1-dinitroethane. It was anticipated that elimination-addition would occur (Equation 13) in a manner analogous to that of 1,1,1-trinitroethane. It was found, however, that

$$2C_5H_{10}NH + CH_3\text{-}CBr(NO_2)_2 \longrightarrow C_5H_{10}N\text{-}CH_2\text{-}CH(NO_2)_2 + C_5H_{10}NH{\cdot}HBr \qquad (13)$$

oxidation-reduction involving displacement of bromonium ion occurred to give the piperidine salt of 1,1-dinitroethane in excellent yield (Equation 14); the other products of reaction, as yet, are unidentified.

$$C_5H_{10}NH + CH_3\text{-}CBr(NO_2)_2 \xrightarrow{CH_3OH} C_5H_{10}\overset{+}{N}H_2\,(O_2N)_2\overset{-}{C}\text{-}CH_3 + [HOBr] \qquad (14)$$

Piperidium 1,1-dinitroethane was identified (tentative) by independent synthesis from piperidine and 1,1-dinitroethane (89 %); the two products have similar chemical properties and identical ultra-violet absorption characteristics (see Experimental). X-ray crystallographic studies of these products are now in progress.

4. REACTIONS OF SILVER 1,1-DINITROETHANE WITH ALKYL HALIDES

Reaction of silver salts of acidic nitro compounds with alkyl or substituted benzyl halides may lead either to carbon or oxygen alkylated products. Reaction of silver nitroform with methyl iodide gives the carbon alkylated product, 1,1,1-trinitroethane, in near quantitative yield;[6] substituted benzyl halides are reported to give both carbon and oxygen alkylated derivatives.[7] Recent investigations with silver nitroform dissolved in dry acetonitrile[8] indicate that carbon alkylation of primary alkyl halides is a fairly general reaction in that 1,1,1-trinitroalkanes are formed in yields up to 65%. Reaction of silver salts of mononitro compounds with alkyl halides may lead to a mixture of carbon or oxygen-alkylated products; silver ethyl nitroacetate reacts with methyl or ethyl iodide to give 22-28% yields of carbon alkylated product,[9] but the major products are unstable oxygen alkylated derivatives. Other examples of reactions of this type have been reported.[10]

The action of alkyl halides on salts of acidic 1,1-dinitroalkanes has been studied by Duden[11] and Nef.[12] Duden reports that silver dinitromethane reacts with methyl and ethyl iodide to give only carbon alkylated products (no yields given). Nef, however, investigated the actions of methyl and ethyl iodide on silver 1,1-dinitroethane carefully and concluded that the reaction courses are very complex. The products formed, when methyl iodide was reacted in the absence of a solvent, were 2,2-dinitropropane (9.5%), 1,1-dinitroethane (15.2%), ethylnitrolic acid (6.1%), formaldehyde (odor) and a neutral oil believed to be methyl ethanenitrolate. The following equations were proposed to explain formation of the products (Equations 15, 16, 17, 18 and 19):

$$CH_3\text{-}C(NO_2)_2Ag + CH_3I \longrightarrow CH_3\text{-}C(NO_2)_2\text{-}CH_3 + AgI \qquad (15)$$

$$CH_3\text{-}C(NO_2)_2Ag + CH_3I \longrightarrow CH_3\text{-}C(NO_2){=}NO_2CH_3 + AgI \qquad (16)$$

$$CH_3\text{-}C(NO_2){=}NO_2CH_3 \longrightarrow CH_3\text{-}C(NO_2){=}NOH + CH_2O \qquad (17)$$

$$CH_3\text{-}C(NO_2)_2Ag + CH_3\text{-}C(NO_2){=}NOH \longrightarrow CH_3\text{-}CH(NO_2)_2 + CH_3\text{-}C(NO_2){=}NOAg \qquad (18)$$

$$CH_3\text{-}C(NO_2){=}NOAg + CH_3I \longrightarrow CH_3\text{-}C(NO_2){=}NOCH_3 + CH_3I \qquad (19)$$

The purpose of the present investigation is to study the effects of temperature and solvents of high dielectric constant (e.g., acetonitrile, dimethyl formamide) on reactions of alkyl halides and silver salts of mono and dinitroalkanes in an effort to favor displacements of the carbon-alkylation type. The system selected for initial study is methyl iodide and silver 1,1-dinitroethane at 0-5° in anhydrous acetonitrile.

The reaction products consist of both neutral and acidic components; separation may be made by alkaline extraction or by chromatographic adsorption. The neutral fraction does not crystallize well and thus was steam-distilled. 2,2-Dinitropropane was obtained in 13.7 per cent overall yield; however, the handling losses were over 60 per cent. Efforts are being directed toward improving both the reaction conditions and the purification procedure. The alkali-soluble components consist of 1,1-dinitroethane (9.8%), formaldehyde, and a crystalline white product (very high melting point) as yet unidentified; no ethylnitrolic acid has been found.

The reactions of silver 1,1-dinitroethane with allyl, higher alkyl, and arylalkyl halides will be reported in a subsequent communication.

5. SELECTIVE REDUCTION OF ALIPHATIC NITRO ALDEHYDES, KETONES, ESTERS, AND ACID CHLORIDES WITH SODIUM TRIMETHOXYBOROHYDRIDE; PREPARATION OF ALIPHATIC NITRO ALCOHOLS AND ALDEHYDES.

It has been previously reported[13] that selective reduction of aliphatic mono and polynitroaldehydes and ketones of all representative structures may be effected with either aluminum isopropoxide or sodium borohydride (acidic, neutral, or basic) to give the corresponding mono or polynitrocarbinols. Similarly, aliphatic nitrocarbinols may be prepared in excellent yields by selective reduction of (1) the corresponding acid chlorides with sodium borohydride[14] and (2) the corresponding alkyl esters with either lithium borohydride[15] in refluxing tetrahydrofuran or lithium aluminum hydride at low temperatures (-80 to -35°).[16] It is now reported that aliphatic mono and polynitro aldehydes, ketones, and esters are reduced to their corresponding carbinols in excellent yields by the action of sodium trimethoxyborohydride.

Sodium or lithium trimethoxyborohydride may be prepared conveniently by reaction of sodium or lithium hydride with trimethylborate[17] (Equation 20)

$$NaH + (CH_3O)_3B \longrightarrow Na(CH_3O)_3BH \qquad (20)$$

in tetrahydrofuran (see Experimental); sodium trimethoxyborohydride may also be purchased from Metal Hydrides Incorporated. Sodium trimethoxyborohydride offers advantage over sodium borohydride in that it is much more soluble in organic solvents, it is a more powerful reducing agent, and it offers the possibility for controlled reductions involving transfer of only one hydride ion.

Reduction of 4-methyl-4-nitro-1-pentanal and 5,5-dinitro-2-hexanone occurs very rapidly with sodium trimethoxyborohydride at room temperature to give 4-methyl-4-nitro-1-pentanol (90% yield) and 5,5-dinitro-2-hexanol (89% yield). These reductions compare favorably with those with sodium borohydride; use of sodium trimethoxyborohydride may offer advantage over sodium borohydride in that it is potentially a cheaper reagent.

Sodium trimethoxyborohydride offers advantage over sodium borohydride in that it can be used efficiently for selective reduction of aliphatic nitro esters to the corresponding nitroalcohols. Reduction of methyl 4-methyl-4-nitropentanoate and methyl 4-nitrobutanoate is effected readily by sodium trimethoxyborohydride in refluxing tetrahydrofuran to yield 4-methyl-4-nitro-1-pentanol (92%) and 4-nitro-1-butanol (80%). The efficiency of reduction of aliphatic nitro esters with sodium trimethoxyborohydride is comparable to that obtained with lithium borohydride. Sodium trimethoxyborohydride may be more feasible as an industrial reducing agent than lithium borohydride in that it can possibly be manufactured at a lower cost.

Sodium trimethoxyborohydride has been shown to reduce acid chlorides of carboxylic acids to aldehydes if only equivalent quantities of reducing agent are used (Equation 21).[17]

$$R\text{-}\overset{O}{\overset{\|}{C}}\text{-}Cl + NaHB(OCH_3)_3 \longrightarrow R\text{-}CH{=}O + NaCl + B(OCH_3)_3 \qquad (21)$$

It is now reported that aromatic and representative aliphatic mono and polynitro acid chlorides may be reduced to their corresponding nitro aldehydes by reaction with sodium trimethoxyborohydride in tetrahydrofuran at -40 to -30°. Reduction of p-nitrobenzoyl chloride, 4-methyl-4-nitropentanoyl chloride, 4,4-dinitropentanoyl chloride, 4-nitropentanoyl chloride, and 4-nitrobutanoyl chloride result in convenient formation of p-nitrobenzaldehyde (74% yield), 4-methyl-4-nitropentanal (66% yield), 4,4-dinitropentanal (72% yield), 4-nitropentanal (63% yield) and 4-nitrobutanal (36% yield). 4-Methyl-4-nitropentanoyl chloride was obtained in 98 per cent yield by reaction of thionyl chloride and 4-methyl-4-nitropentanoic acid; 4-methyl-4-nitropentanoic acid (84.5% yield) was prepared by hydrolysis of methyl 4-methyl-4-nitropentanoate, with refluxing hydrochloric acid. 4,4-Dinitropentanoyl chloride is formed in 88 per cent yield from 4,4-dinitropentanoic acid and thionyl chloride. 4-Nitropentanoic acid (47.5% yield) and 4-nitrobutanoic acid (26% yield) were prepared by saponification of methyl 4-nitropentanoate and methyl 4-nitrobutanoate with cold aqueous-methanolic sodium hydroxide. 4-Nitrobutanoyl chloride and 4-nitropentanoyl chloride were obtained by reaction of 4-nitrobutanoic acid and 4-nitropentanoic acid with phosphorus trichloride in 86 per cent and 83 per cent yields, respectively; no appreciable chlorination of the acidic nitro groups occurred in these reactions.

6. SELECTIVE REDUCTION OF 2-METHYL-1-NITROPROPENE WITH SODIUM TRIMETHOXYBOROHYDRIDE; 2-METHYL-1-NITROPROPANE.

Sodium trimethoxyborohydride has been found to be an excellent selective agent for reduction of carbon-carbon double bonds in conjugated nitroolefins. 2-Methyl-1-nitropropene has been reduced to 2-methyl-1-nitropropane in 63.4 per cent yield in ethyl ether-tetrahydrofuran at

-5 to 0° (Equations 22, 23); 2-methyl-1-nitropropane may be isolated upon

$$(CH_3)_2C{=}CHNO_2 + NaHB(OCH_3)_3 \longrightarrow (CH_3)_2CH\text{-}CHNO_2Na + (CH_3O)_3B \quad (22)$$

$$(CH_3)_2CH\text{-}CHNO_2Na + H^+ \xrightarrow{urea} (CH_3)_2CH\text{-}CH_2NO_2 + Na^+ \quad (23)$$

acidifying the reduction mixture with urea-acetic acid. The products of reaction other than 2-methyl-1-nitropropane are unreacted 2-methyl-1-nitropropene and a high boiling product believed to be 1,3-dinitro-2,2,4-trimethylpentane, derived by Michael addition of sodium 2-methyl-1-nitropropane to 2-methyl-1-nitropropene (Equation 24).

$$(CH_3)_2CH\text{-}CHNO_2Na + (CH_3)_2C{=}CHNO_2 \longrightarrow (CH_3)_2CH\text{-}CH(NO_2)\text{-}C(CH_3)_2\text{-}CHNO_2Na \quad (24)$$

A study of the effect of temperature (0 to 34°) and reaction time (2 to 20 hours, see Experimental) has shown that the desired addition reaction proceeds optimally at the lower temperatures and when the reaction period is not prolonged.

2-Methyl-1-nitropropane was identified by its physical constants, its infrared spectrum, and by conversion to 2-methyl-1-propanal via the Nef reaction[18] and thence to 2-methyl-1-propanal 2,4-dinitrophenylhydrazone.

7. REDUCTION OF 2-METHYL-1-NITROPROPENE WITH LITHIUM BOROHYDRIDE; 2-METHYL-1-NITROPROPANE.

Selective reduction of the olefinic double in conjugated nitroalkanes may be effected with lithium borohydride in ethyl ether-tetrahydrofuran; reaction of 2-methyl-1-nitropropene with lithium borohydride at -5 to 0° gave 2-methyl-1-nitropropane in 48.4 per cent yield (Equations 25 and 26) upon acidification with urea-acetic acid.

$$4\,(CH_3)_2C{=}CHNO_2 + LiBH_4 \longrightarrow \left((CH_3)_2CH\text{-}CHNO_2\right)_4BLi \quad (25)$$

$$\left((CH_3)_2CH\text{-}CHNO_2\right)_4BLi + HAc + 3H_2O \longrightarrow 4(CH_3)_2CH\text{-}CH_2NO_2 + LiAc + H_3BO_3 \quad (26)$$

It is believed that the yields from these reactions can be greatly increased upon further experimentation. 2-Methyl-1-nitropropane was identified by its chemical and physical properties, its infrared spectrum, and by conversion to 2-methylpropanal[18] and its 2,4-dinitrophenylhydrazone.

Since either lithium borohydride or sodium trimethoxyborohydride may be used for selective reduction of the carbon-carbon double bond of conjugated nitroolefins, selection of the reagent is determined by the availability and cost of the reducing agents. At present, lithium borohydride is much cheaper than sodium trimethoxyborohydride per mole of available hydrogen; however, sodium trimethoxyborohydride has the advantage of either being more readily available commercially or can be more easily prepared in the laboratory.

8. REACTION OF 2-NITRO-1-BUTYL ACETATE WITH LITHIUM BOROHYDRIDE OR SODIUM TRIMETHOXYBOROHYDRIDE; 2-NITRO-1-BUTANOL.

The reactions of 2-nitro-1-butyl acetate with either lithium borohydride or sodium trimethoxyborohydride have been investigated as a direct method for preparation of saturated nitroalkanes. It was deemed possible that either sodium trimethoxyborohydride or lithium borohydride would effect elimination of acetic acid from 2-nitro-1-butyl acetate to 2-nitro-1-butene; subsequent reduction of 2-nitro-1-butene with sodium trimethoxyborohydride or lithium borohydride is expected to yield 2-nitrobutane (Equations 27 and 28). A reduction sequence of this type would eliminate one step in the preparation of nitroalkanes from vicinal nitroalcohols since nitroolefins are usually prepared by elimination of acetic acid (or its homologs) from vicinal acetoxynitroalkanes.

$$CH_3\text{-}CH_2\text{-}CH(NO_2)\text{-}CH_2\text{-}O_2C\text{-}CH_3 \xrightarrow[\text{2. }NaHB(OCH_3)_3]{\text{1. }LiBH_4} CH_3\text{-}CH_2\text{-}C(NO_2)\text{=}CH_2 + CH_3CO_2H \qquad (27)$$

$$CH_3\text{-}CH_2\text{-}C(NO_2)\text{=}CH_2 \xrightarrow[\text{2. }NaHB(OCH_3)_3]{\text{1. }LiBH_4} CH_3\text{-}CH_2\text{-}CH(NO_2)\text{-}CH_3 \qquad (28)$$

Reaction of 2-nitro-1-butyl acetate with sodium trimethoxyborohydride or with lithium borohydride at 3-5° resulted in reduction of the acetate ester to yield 2-nitro-1-butanol and ethanol; the yields of 2-nitro-1-butanol ranged from 40 to 60 per cent (Equation 29). No evidence was obtained for the formation of 2-methyl-1-nitrobutane. It may be concluded

$$CH_3\text{-}CH_2\text{-}CH(NO_2)\text{-}CH_2\text{-}O_2C\text{-}CH_3 \xrightarrow[\text{2. }NaHB(OCH_3)_3]{\text{1. }LiBH_4} CH_3\text{-}CH_2\text{-}CH(NO_2)\text{-}CH_3 + CH_3\text{-}CH_2OH \qquad (29)$$

therefore that neither lithium borohydride nor sodium trimethoxyborohydride are sufficiently strong bases to effect elimination of acetic acid from 2-nitro-1-butyl acetate and thus normal reduction of the nitro ester to the nitro alcohol occurs. Selective-reduction of vicinal nitroalkyl esters with lithium borohydride or with sodium trimethoxyborohydride will be investigated further in the presence of strong bases such as metal alkoxides in an effort to effect reduction of the elimination-addition type.

9. PREPARATION AND OXIDATIVE-NITRATION OF 2-METHYL-1-NITROPROPANE, 1-NITROPENTANE, 3-METHYL-1-NITROBUTANE, 3,3-DIMETHYL-1-NITROBUTANE, AND CYCLOHEXYLNITROMETHANE; 1,1-DINITRO-2-METHYLPROPANE, 1,1-DINITROPENTANE, 1,1-DINITRO-3-METHYLBUTANE, 3,3-DIMETHYL-3,3-DINITROBUTANE AND CYCLOHEXYLDINITROMETHANE.

Highly purified samples of 2-methyl-1-nitropropane (70%), 1-nitropentane (39 %), 3-methyl-1-nitrobutane (61%), and 3,3-dimethyl-1-nitrobutane (23 %) were prepared by reaction of silver nitrate with 1-iodo-2-methylpropane, 1-bromopentane, 1-bromo-3-methylbutane and 1-bromo-3,3-dimethylbutane respectively. 1-Bromo-3,3-dimethylbutane was obtained by reaction of tert-butyl bromide with ethylene in the presence of aluminum bromide.[19] Oxidative-nitration of 2-methyl-1-nitropropane, 1-nitropentane, 3-methyl-1-nitrobutane, 3,3-dimethyl-1-nitrobutane, and cyclohexylnitromethane (obtained from Dr. N. Kornblum) in alkaline solution with silver nitrate and sodium nitrite gave 1,1-dinitro-2-methylpropane (55%), 1,1-dinitropentane (75%), 1,1-dinitro-3-methylbutane (61%), 3,3-dimethyl-3,3-dinitrobutane (43%) and cyclohexyldinitromethane (65%). The 1,1-dinitroalkanes were purified by recrystallization of their potassium salts, regeneration by the action of acetic acid, and fractional distillation at reduced pressure under nitrogen. The highly purified 1,1-dinitroalkanes were characterized by quantitative and infrared analyses, neutral equivalents, molecular refractions, and by analysis of their potassium and silver derivatives.

10. PHYSICAL PROPERTIES AND STRUCTURES OF 1,1-DINITROALKANES

It has previously been reported[2] from this laboratory that 1,1-dinitroalkanes branched in the alpha position exhibit behavior which is atypical of normal 1,1-dinitroalkanes in that (1) they are much weaker acids (2) their ultraviolet absorption spectra become more similar to those of primary mononitro compounds and (3) their potassium salts are much more soluble in water and in methanol. In attempting to explain the differences in physical properties of normal and substituted 1,1-dinitroalkane anions, it was suggested that resonance interaction in unbranched 1,1-dinitroalkane anions occurs extensively with both nitro groups resulting in a coplanar aci-dinitro system, whereas in 1,1-dinitroalkanes which are branched in the alpha position the steric requirements of the hindering groups are such that the resonating aci-dinitro system can not become coplanar and thus the principal stabilizing interaction possibly occurs with only one nitro group. It is thus to be expected that 1,1-dinitroalkanes which are highly branched in the alpha position resemble primary mononitro alkanes; secondly, a sounder understanding of the influence of substituents on the structure of 1,1-dinitroalkane anions may result in more effective control of carbon and oxygen alkylation reactions of acidic mono and polynitroalkanes.

In the present investigation the ionization constants of a series of highly purified 1,1-dinitroalkanes, including 1,1-dinitropentane, 1,1-dinitro-3-methylbutane, 3,3-dimethyl-1,1-dinitrobutane, and cyclohexyldinitromethane, have been determined in methanol (17.8% and 44.3% by weight) - water at 25.0 ± 0.1°. The data now being reported (Table 1) are believed to be more quantitative than that previously described.[2]

The ionization constants of a series of 1,1-dinitroalkanes in 17.8% methanol and in 44.3% methanol were determined (Table 1) in order to establish (1) the effect of dielectric nature of the solvent system on the acid strength of 1,1-dinitroalkanes and (2) the relative orders of strengths of 1,1-dinitroalkanes in solvent mixtures of different dielectric constants. It was found throughout this study that the acid strengths of 1,1-dinitroalkanes were significantly less in 44.3% methanol than in 17.8% methanol. Similar behavior has been demonstrated previously with other acid systems; it is now apparent that pseudo acids of the 1,1-dinitroalkane type parallel the behavior of other acids in that their ionizations are repressed in solvents of low dielectric constants. (A study of the ionization constants of phenyldinitromethane at 25° as a function of the dielectric constants of mixtures of methanol and water reveals that the acid strengths of phenyldinitromethane obey a linear relation over the dielectric constant range: 59.0 to 71.0 (Table 2); further research is in progress to determine if this simple relationship exists in solvent systems of low dielectric constant). Secondly, the relative order of acid-strengths of the various 1,1-dinitroalkanes in 44.3% methanol parallels that found in 17.8% methanol; it is thus believed that the apparent order of acid strengths that have been obtained for the 1,1-dinitro-alkanes are primarily characteristic of the dinitro acids and not the particular solvent system.

The results of the present investigation reveal that normal (unbranched) 1,1-dinitroalkanes such as 1,1-dinitropropane, 1,1-dinitrobutane and 1,1-dinitropentane are acids of similar strengths (K_{ion} 2.2 to 3.5 x 10^{-6}). 1,1-Dinitropropane is a slightly weaker acid than 1,1-dinitrobutane and 1,1-dinitropentane (it is believed that the differences observed are real); the unexpected weaker acid strength of 1,1-dinitropropane than 1,1-dinitrobutane and 1,1-dinitropentane parallels that for aliphatic carboxylic acids (K_{ion} propionic acid 1.3 x 10^{-5}; K_{ion} butyric acid 1.5 x 10^{-5} and K_{ion} pentanoic acid 1.5 x 10^{-5}). Since on the basis of the usual inductive effects of alkyl groups it would be predicted that 1,1-dinitrobutane and 1,1-dinitropentane would be weaker acids than 1,1-dinitropropane, it is suggested that the relatively greater acid strengths of 1,1-dinitro-butane and 1,1-dinitropentane arise from their greater steric requirements (B-strain) and entropy factors.

Table 1

IONIZATION CONSTANTS AND NEUTRALIZATION DATA FOR SUBSTITUTED 1,1-DINITROALKANES AT 25.0 ± 0.1°C IN METHANOL (17.8 ± 0.1%)-WATER AND METHANOL (44.3 ± 0.1%)-WATER

	% MeOH at 1/2 titre[b,c]	Neut. Equiv.		pKa	Ka	% MeOH at 1/2 titre[c,d]	Neut. Equiv.		pKa	Ka
		Calc'd.	Found				Calcd.	Found		
1. CH_3-CH_2-$CH(NO_2)_2$	17.8 ± 0.1	134	134	5.66	$2.2 \pm 0.2 \times 10^{-6}$	44.2 ± 0.1	134	135	6.21	$6.2 \pm 0.1 \times 10^{-7}$
2. CH_3-CH_2-CH_2-$CH(NO_2)_2$	17.8 ± 0.1	148	150	5.45	$3.5 \pm 0.05 \times 10^{-6}$	44.3 ± 0.1	148	149	5.90	$1.2 \pm 0.05 \times 10^{-6}$
3. CH_3-CH_2-CH_2-CH_2-$CH(NO_2)_2$	17.8 ± 0.1	162	163	5.52	$3.0 \pm 0.05 \times 10^{-6}$	44.2 ± 0.1	162	161	5.92	$1.2 \pm 0.1 \times 10^{-6}$
4. CH_3-$CH(CH_3)$-$CH(NO_2)_2$	17.8 ± 0.1	148	150	6.92	$1.2 \pm 0.1 \times 10^{-7}$	44.3 ± 0.1	148	148	7.42	$3.8 \pm 0.20 \times 10^{-8}$
5. CH_3—$C(CH_3)(CH_3)$—$CH(NO_2)_2$	17.8 ± 0.1	162	162	8.25	$5.6 \pm 0.05 \times 10^{-9}$	44.3 ± 0.1	162	162	8.77	$1.7 \pm 0.05 \times 10^{-9}$
6. CH_3-$CH(CH_3)$-CH_2-$CH(NO_2)_2$	17.8 ± 0.1[e]	162	161	5.68	$2.1 \pm 0.1 \times 10^{-6}$	44.3 ± 0.1	162	162	6.05	$8.9 \pm 0.05 \times 10^{-7}$
7. Ø-$CH(NO_2)_2$	17.7 ± 0.1[e]	182[f]	171[f]	4.32	$4.8 \pm 0.2 \times 10^{-5}$	44.3 ± 0.1	182[f]	171[f]	4.78	$1.6 \pm 0.2 \times 10^{-5}$
8. $C_6H_{11}CH(NO_2)_2$	17.8 ± 0.1[e]	188	187	7.35	$4.5 \pm 0.1 \times 10^{-8}$	44.3 ± 0.1	188	187	7.39	$4.1 \pm 0.1 \times 10^{-8}$
9. Ø-CO_2H	17.8 ± 0.1	122	122	4.42	$3.8 \pm 0.05 \times 10^{-5}$	44.3 ± 0.1	122	121	5.15	$7.1 \pm 0.05 \times 10^{-6}$
10. CH_3-$C(CH_3)_2$-CH_2-$CH(NO_2)_2$						44.2 ± 0.1	176	178	5.55	$2.8 \pm 0.05 \times 10^{-6}$
11. CH_3-CH_2-O-CH_2-$CH(NO_2)_2$	17.9 ± 0.1	164	181[f]	3.98	$1 \pm 0.1 \times 10^{-4}$					

a. The temperature of all solutions were 25.0 ± 0.1 C. Titrations were conducted with a Beckman pH meter (glass electrode), standardized with an acetic acid-sodium acetate buffer (pH = 4) in water. b. Neutralizations were conducted by adding 0.1000 N sodium hydroxide to a solution of the 1,1-dinitroalkane in a mixture of 15 ml. of c.p. methanol and 50 ml. of distilled water at 25°. c. Per cent methanol by weight. d. Titrations were conducted by adding 0.1000 N sodium hydroxide in 50:50 methanol-water (by volume at 25°) to a solution of the 1,1-dinitroalkane in 50:50 methanol-water (by volume) at 25°.
e. Compounds were not completely soluble in 15:50 methanol-water at outset of titrations. f. Neutralization equivalent data are unsatisfactory; impurities do not affect pKa or K_{ion} values significantly.

It has also been found that substituents in the beta position do not have important effects on the acid strength of 1,1-dinitroalkanes or on the ultra-violet absorption characteristics and the solubilities of potassium salts of 1,1-dinitroalkanes (Tables 1, 3 and 4), 1,1-Dinitro-3-methylbutane and 3,3-dimethyl-1,1-dinitrobutane anions have ionization, ultraviolet, and solubility characteristics which are similar to those of unbranched 1,1-dinitroalkanes (Tables 1, 3 and 4), and thus it may be concluded that steric requirements of substituents in the beta-position do not hinder normal resonance stabiliaation of the nitro-nitronate ion.

2,2-Dimethyl-1,1-dinitropropane and 1,1-dinitro-2-methylpropane give evidence for being "strained" 1,1-dinitroalkanes (Table 1, see reference 2 for a more complete resumé of the evidence). It has now been established that cyclohexyldinitromethane is a stronger acid than 2,2-dimethyl-1,1-dinitropropane (Table 1); however, it is a weaker acid than normal 1,1-dinitroalkanes. It has also been observed that the ultraviolet and the solubility characteristics of cyclohexyldinitromethane anions are intermediate to that observed for normal and highly hindered 1,1-dinitroalkane anions. The properties of cyclohexyldinitromethane thus appear to be in accord with that expected for the steric requirements of the cyclohexane ring.

Table 2

THE EFFECT OF SOLVENT COMPOSITION AND DIELECTRIC CONSTANT ON THE IONIZATION CONSTANT OF PHENYLDINITROMETHANE AT 25.0 ± 0.1°.

ml. MeOH in 50 ml. H_2O	% MeOH by weight	Dielectric Constant	K_{ion}
15	17.58	71.0	4.8×10^{-5}
30	29.76	65.5	3.4×10^{-5}
40	36.30	62.8	2.5×10^{-5}
50	44.00	59.0	1.6×10^{-5}

Albright and Gosting, J. Am. Chem. Soc., 68, 1061 (1949).

Table 3

EFFECT OF STRUCTURE ON THE ULTRAVIOLET ABSORPTION OF SUBSTITUTED 1,1-DINITRO ANIONS

Anion[a]	Max. 1		Min. 1		Max. 2	
	mμ	log ε	mμ	log ε	mμ	log ε
$CH_3-CH_2-CH_2-CH_2-C(NO_2)_2^-$	384	4.18	304	2.94	227	3.84
$(CH_3)_2CH-CH_2-C(NO_2)_2^-$	384	4.12	304	2.81	229	3.79
$(CH_3)_3C-CH_2-C(NO_2)_2^-$	384	4.14	306	2.83	228-9	3.88
$C_6H_{11}-C(NO_2)_2^-$	386	3.95	304	2.94	232	3.95

a. The solutions were prepared by dissolving potassium salts of the 1,1-dinitroalkanes in 1.0 x 10^{-3} N sodium hydroxide. The concentrations of all salts of 1,1-dinitroanions were 1.000 x 10^{-4} molar.

Table 4

SOLUBILITIES OF POTASSIUM 1,1-DINITROALKANES

Compound Potassium salt of	Solubility in water	Temp. °C.
1,1-Dinitropentane	1 part in 36	25
1,1-Dinitro-3-methylbutane	1 part in 6.0	26
3,3-Dimethyl-1,1-dinitrobutane	1 part in 15.3	32
Cyclohexyldinitromethane	1 part in 34.3	24

11. BASE-CATALYZED ADDITION REACTIONS OF 2-NITROPROPANE AND 1,1-DINITROETHANE WITH METHYL PROPIOLATE; METHYL 4-METHYL-4-NITRO-2-PENTENOATE.

The base-catalyzed reactions of acidic mono and dinitroalkanes with methyl propiolate are being studied as new Michael systems which may be of value in the nitropolymer program. Addition of alpha-omega dinitro or polynitroalkanes to methyl propiolate should lead to a series of difunctional intermediates which may be of particular value in the synthesis of solid propellants.

Methyl propiolate[20] has been prepared in 60 per cent yield by esterification of propiolic acid with methanol in sulfuric acid at room temperature. Propiolic acid (32% yield) was obtained by decarboxylation of potassium acid acetylenedicarboxylate in warm water and subsequent acidification of the reaction mixture.[21] Acetylenedicarboxylic acid was synthesized by the following sequence: (1) bromination of fumaric acid to give 2,3-dibromosuccinic acid[22] and (2) dehydrohalogenation of 2,3-dibromosuccinic acid with refluxing aqueous potassium hydroxide.[23]

Reaction of 2-nitropropane and methyl propiolate at 0 to 25° in the presence of sodium methoxide occurred readily to give methyl 4-methyl-4-nitro-2-pentenoate in 55.4 per cent yield (Equation 30). Methyl 4-methyl-4-nitro-2-pentenoate is a stable oily liquid which was

$$(CH_3)_2CH\text{-}NO_2 + CH{\equiv}C\text{-}CO_2CH_3 \xrightarrow{CH_3ONa} (CH_3)_2C(NO_2)\text{-}CH{=}CH\text{-}CO_2CH_3 \quad (30)$$

identified by its chemical properties, infrared spectrum, and quantitative analysis.

Reaction of 1,1-dinitroethane and methyl propiolate has been investigated in the presence of benzyltrimethylammonium hydroxide. Addition occurs very rapidly to give presumably methyl 4,4-dinitro-2-pentenoate (Equation 31); the addition is exothermic and, unless

$$CH_3\text{-}CH(NO_2)_2 + CH_2{=}CH\text{-}CO_2CH_3 \xrightarrow{NaOMe} CH_3\text{-}C(NO_2)_2\text{-}CH{=}CH\text{-}CO_2CH_3 \quad (31)$$

the initial reaction mixture is cooled sufficiently, fume-offs may occur. The crude adduct is a liquid which is thermally unstable, and as yet all efforts to effect its purification by distillation or crystallization have been unsuccessful. Further attempts to purify and characterize this reaction product are now in progress.

Future research in this area will include a study of the reactions of nitromethane, nitroethane, dinitromethane and trinitromethane with methyl propiolate.

12. REACTION OF METHYL MAGNESIUM IODIDE AND 2-METHYL-1-NITROPROPENE AND REDUCTIVE DIMERIZATION; 2,2-DIMETHYL-1-NITROPROPANE AND 1,4-DINITRO-2,2,3,3-TETRAMETHYLBUTANE.

It has been previously reported[1,2,15] that reaction of methyl magnesium iodide and 2-methyl-1-nitropropene yields, in addition to 2,2-dimethyl-1-nitropropane (Equation 32), 1,4-dinitro-2,2,3,3-tetramethylbutane (Equation 33).

$$(CH_3)_2C{=}CHNO_2 \xrightarrow[2.\ H_2O]{1.\ CH_3MgI} (CH_3)_3\text{-}CH_2NO_2 \qquad (32)$$

$$2(CH_3)_2C{=}CHNO_2 + 2H\cdot \xrightarrow[2.\ H_2O]{1.\ CH_3MgI} O_2NCH_2\text{-}C(CH_3)_2\text{-}C(CH_3)_2\text{-}CH_2NO_2 \qquad (33)$$

In an effort to gain information concerning the nature of the reductive-dimerization process, a study has been initiated of the effects of temperature and time on reactions of 2-methyl-1-nitropropene and methyl magnesium iodide. The results of the recent studies are summarized in Table 5. In general, low temperatures and long reaction periods hinder reductive-dimerization of 2-methyl-1-nitropropene; during long reaction periods and, in particular, at the lower temperatures, a third product (a high-melting, white, crystalline solid), as yet unidentified (see Experimental, no nitro groups are present in the product), has been isolated. Further results of this study will be reported in subsequent communications from this laboratory.

Table V

REACTION OF 2-METHYL-1-NITROPROPENE AND METHYL MAGNESIUM IODIDE

Reaction Time, Hrs.	Temp., °C	Yield, % 2,2-Dimethyl-1-Nitropropane	1,4-Dinitro-2,2,3,3-tetramethylbutane	Solid A*
0.25	0	40.4	6.2	0.0
3.0	0	37.7	1.9	4.5
3.0	-25	48.2	2.4	7.1
3.5	-65	35.0	1.3	8.4

* Unidentified, described in experimental section.

1. **REACTION OF N-BUTYLLITHIUM WITH 1,1,1-TRINITROETHANE IN BENZENE; LITHIUM 1,1-DINITROETHANE.**

(a) Preparation of n-butyllithium: A Grignard flask (500 ml.) fitted with a nitrogen inlet tube, a stirrer and a dropping funnel was flamed out and allowed to cool in a dry nitrogen atmosphere. The flask was charged with lithium shot (4.5 g. ca. 0.6 gm. atom) and dry benzene (100 ml.). n-Butyl bromide (34.3 g., 0.30 mole) in benzene (100 ml.) was added slowly at room temperature until reaction began. The mixture was then cooled in an ice-water bath while the remaining bromide was added (30 min.). The mixture was stirred for another hour, then was transferred, under nitrogen pressure, into a dry centrifuge bottle. The suspension was centrifuged at 1900 r.p.m. for 15 minutes; the clear supernatant liquid was then transferred, under nitrogen pressure, into a dry, nitrogen-flushed reaction flask.

(b) Reaction with 1,1,1-trinitroethane: A solution of 1,1,1-trinitroethane (16.5 g., 0.10 mole) in dry benzene (40 ml.) was added dropwise (2 hours) to the stirred n-butyllithium solution at 5°. After the pale-red reaction mixture had been stirred for another hour, water was added to decompose the excess n-butyllithium and to dissolve the salt products. The benzene layer was extracted several times with water, the aqueous layers being collected in a 1-liter volumetric flask. The flask was filled to volume with water; this solution at maximum theoretical concentration is 0.100 M lithium 1,1-dinitroethane. For ultraviolet analysis, the solution was diluted 1:1000 with water; three separate samples of this concentration were prepared and analyzed. For comparison, two samples of 1.00×10^{-4} M potassium 1,1-dinitroethane (in 10^{-3} N sodium hydroxide) were also analyzed. The results follow:

(I) Potassium 1,1-dinitroethane

Sample	Maximum(mμ)	E_{max}	$k \left[= \frac{E\ max}{cd}\right]$
1	381	1.65	16500
2	381	1.62	16200
		Average	16350 (± 150)

(II) Unknown (lithium 1,1-dinitroethane)

Sample	Maximum (mμ)	E max	d (cm)	$c = \left[\frac{E\ max}{kd}\right]$
1	381	0.277	1.00	1.69×10^{-5} M
2	378-381	0.283	1.005	1.72×10^{-5} M
3	381	0.278	1.00	1.70×10^{-5} M
			Average	$1.70 \pm 0.01 \times 10^{-5}$ M

Therefore, the conversion of 1,1,1-trinitroethane to lithium 1,1-dinitroethane was 17.0% (± 0.1%).

The benzene layer was evaporated nearly to dryness. Petroleum solvent was added and, on continued evaporation, white crystals of 1,1,1-trinitroethane separated. The crystals were filtered and the filtrate again evaporated, etc., until no more crystals were obtained. A residual oil (ca. 2 ml.) was discarded. The recovery of 1,1,1-trinitroethane was 6.37 g. (0.0386 mole = 38.6% recovery).

2. REACTION OF GUANIDINE WITH 1,1,1-TRINITROETHANE (IMPROVED PROCEDURE)

A solution of guanidine (ca. 0.20 mole) in absolute alcohol was prepared as previously described.[15] The guanidine-alcohol solution was stirred at 0-5° while 1,1,1-trinitroethane (8.25 g., 0.05 mole) in absolute ethanol (40 ml.) was added dropwise (70 minutes). When the addition had been almost completed, a yellow precipitate of 2,2-dinitroethyl-guanidine separated from solution. The solution was stirred at room temperature for 16 hours. The mixture was then stirred in an ice-water bath for 45 minutes and filtered. The yellow-orange salt was washed with absolute alcohol, alcohol-ether, and ether, and sucked dry. The yield of salt was 7.24 g.

The filtrate was evaporated to about half its volume, and additional yellow-orange salt (0.61 g.) was recovered. On continued evaporation of the filtrate, a final 2.11 g. of orange salt was obtained. The total yield of crude product was 9.96 g; the 2,2-dinitroethyl-guanidine content of this salt was determined by ultraviolet analysis. A carefully purified sample of 2,2-dinitroethyl-guanidine, made up to concentrations of 1.00×10^{-4}, 5.00×10^{-5} and 1.00×10^{-5} M (two samples at each conc. in ten-fold excess of base) was used as the standard; the average value found for the molecular extinction coefficient (k) at 364-5 mμ was 16230 (± 50). Over the range of concentrations studied, the compound obeyed Beer's Law. Analysis of two samples of each unknown salt fraction gave the following results:

Salt Fraction	$E_{364-5m\mu}$	d(cm.)	c $\left[= \frac{E_{364-5m\mu}}{kd}\right]$	% Product $\left[= \frac{c}{1 \times 10^{-4}} \times 100\right]$	Weight of Product
1 (7.24 g.)	1.32	1.00	0.812×10^{-4}	81.0 ± 0.3%	5.86 g.
	1.32	1.005	0.809×10^{-4}		
2 (0.61 g.)	0.98	1.00	0.604×10^{-4}	60.1 ± 0.3%	0.37 g.
	0.97	1.00	0.598×10^{-4}		
3 (2.11 g.)	0.486	1.00	0.299×10^{-4}	29.8 ± 0.3%	0.65 g.
	0.484	1.00	0.298×10^{-4}		

The total yield of 2,2-dinitroethyl-guanidine, therefore, is 6.99 g. (77.7%). On the basis of the proposed reaction equation (see Discussion), the remaining material should be guanidinium nitrite. To verify this, part of fraction 3 (1.00 g.) was purified. On heating this material with absolute ethanol (50 ml.), 0.14 g. of insoluble 2,2-dinitroethylguanidine was recovered. Evaporation of the filtrate gave 0.86 g. of a yellow salt mixture (containing ca. 0.16 g. of 2,2-dinitroethylguanidine) melting at 62-128° (evolution of gas at the higher temperature). This salt was again treated with hot absolute ethanol (25 ml.); the nitrite salt obtained weighed 0.81 g. and melted at 109-132° (evolution of gas, dec.). This salt was very soluble in water, soluble in ethanol and insoluble in ether. The melting range indicates that a mixture is present, probably of guanidinium nitrite and nitrosoguanidine (and a small amount of alkylation product). Guanidinium nitrite melts at 76-78.5° (dec. at 120°),[24] whereas nitrosoguanidine explodes at 165°.[25]

The salt product gave the following tests: (I) Liebermann nitrosamine test - positive, verifying the presence of either a nitrosamine group or a nitrite; (II) addition of concentrated sulfuric acid - gas and heat were evolved indicating the presence of a nitrite group and possible absence of the nitrosamine group (nitrosoguanidine explodes on contact with concentrated sulfuric acid); (III) iodine was liberated from an acidified sodium iodide solution (nitrite); (IV) addition of ferrous ammonium sulfate and sodium hydroxide - the filtrate slowly turned blue. The color persisted after 1.5 hours (nitrosoguanidine gives a non-persistant fuchsin color). Further purification and analysis of this salt are still in progress.

3. DETERMINATION OF X-RAY POWDER DIFFRACTION DATA FOR 2,2-DINITROETHYL GUANIDINE AND N-(2,2-DINITROETHYL)-PIPERIDINE.

X-ray powder diffraction data were obtained for two samples of 2,2-dinitroethyl-guanidine and three samples of N-(2,2-dinitroethyl)-piperidine. The data verifies the structure assigned to both compounds. The instrument used for this analysis was a North American-Phillips X-ray Diffraction Camera, Model 5001[a]; chromium radiation (vanadium filter, Cr, K_α = 2.2850 A°) was employed for 19-20 hours at 32 kilovolts and 9-10 milliamperes. The values for d found are tabulated below:

[a] The project is indebted to Dr. Michael Hock and the Cryogenic Laboratory of The Ohio State University for their assistance in obtaining the data tabulated herein.

2,2-Dinitroethyl guanidine

Sample 1[b] d[g] (Relative intensity)[h]		Sample 2[c] d
2.095 (W)		2.101 (W)
2.467 (WW)		2.467 (WW)
2.583 (WW)		2.578 (WW)
2.691 (WW)		2.688 (WW)
3.047 (SS)		3.048 (SS)
3.420 (S)		3.423 (S)
3.700 (S)		3.741 (S)
3.768 (S)	i	
3.831 (S)		3.855 (S)
4.937 (S)		4.970 (M)
6.152 (S)		6.202 (S)

No back reflection

N-(2,2-dinitroethyl)-piperidine

Sample 1[d] d	Sample 2[e] d	Sample 3[f] d
2.037 (WW)	2.041 (WW)	2.059 (WW)
2.286 (W)	2.286 (W)	2.291 (W)
2.358 (WW)	2.358 (WW)	2.358 (WW)
2.419 (WW)	2.422 (WW)	2.421 (WW)
2.515 (W)	- - -	2.510 (W)
2.525 (M)	2.627 (M)	2.627 (M)
2.891 (W)	2.888 (W)	2.893 (W)
2.951 (W)	2.951 (W)	2.954 (W)
3.000 (W)	3.000 (W)	2.999 (W)
3.160 (W)	3.162 (W)	3.161 (W)
3.229 (M)	3.220 (M)	3.226 (M)
3.338 (WW)	3.344 (WW)	- - -
3.442 (M)	3.454 (M)	3.437 (M)
3.611 (W)	3.604 (W)	3.612 (W)
3.674 (W)	3.662 (W)	3.674 (W)
3.942 (SS)	3.942 (SS)	3.934 (S)
4.120 (W)	4.120 (W)	4.117 (W)
4.459 (S)	4.468 (S)	4.461 (S)
4.652 (M)	4.663 (M)	4.644 (M)
4.841 (S)	4.841 (S)	4.853 (S)
5.519 (M)	5.522 (M)	5.477 (M)
5.963 (WW)	5.935 (WW)	- - -
6.142 (WW)	6.152 (WW)	6.142 (WW)
7.896 (S)	7.896 (S)	7.868 (S)
9.723 (W)	9.649 (WW)	9.707 (WW)
11.346 (W)	11.346 (WW)	11.463 (WW)
Back reflection - 2.625 (WW)	2.634 (WW)	2.629 (WW)

b. Prepared by the interaction of guanidine and trimethylammonium-N-(2-nitroethyl-2-nitronate).

c. Prepared from guanidine and 1,1,1-trinitroethane.

d. Prepared from piperidine and 1,1,1-trinitroethane.

e. Prepared from piperidine, formaldehyde and dinitromethane.

f. Prepared by the interaction of piperidine and trimethylammonium-N-(2-nitroethyl-2-nitronate).

g. Calculated from $\lambda_{Cr} = 2.2850\ \mathring{A} = 2d \sin \theta$.

h. Relative intensity is based upon the strongest line being labelled (SS) and the weakest lines being labelled (WW).

i. These lines are intense and very close together; in sample 2, they could not be resolved.

4. ATTEMPTED REACTION OF POTASSIUM BENZYL CYANIDE WITH 1,1,1-TRINITROETHANE; PREPARATION OF POTASSIUM ETHYL 2,2-DINITROETHYL ETHER.

Benzyl cyanide (14.5 g., 0.124 mole) in absolute ethanol (65 ml.) was added rapidly to a stirred solution of potassium (4.7 g., 0.12 mole) in absolute ethanol (200 ml.). A solution of 1,1,1-trinitroethane (8.25 g., 0.0050 mole) in absolute ethanol (30 ml.) was added at a rapid rate (10 minutes) to the mixture of benzyl cyanide and potassium ethoxide in ethanol. The mixture turned red, a precipitate formed and the temperature rose from 18° to 26°. When the addition was completed, the temperature fell to 20°. The mixture was stirred for one hour at room temperature and then cooled to 5°. The orange salt was filtered, washed with absolute ethanol, ethanol-ether and ether, and sucked dry. The yield of product was 13.15 g. On exposure to air, the salt turned red in color. The product was dried to constant weight (13.11 g.) in a vacuum desiccator.

The crude salt (1.00 g.) was recrystallized from a warm solution of methanol (1.2 ml.) and water (0.7 ml.); a yellow crystalline product of long yellow needles (0.50 g., long needles) was recovered, m.p. 134-136° (dec.). The infrared spectrum of this salt revealed the absence of a nitrile group (no absorption in the region 4-5μ). The ultraviolet spectrum, indicated that the salt was not potassium 1,1-dinitroethane (absorption maximum at 365 mμ instead of at 380-381 mμ). It was concluded that 1,1,1-trinitroethane reacted with ethoxide ion (apparently present in equilibrium with the benzyl cyanide anion) giving potassium ethyl 2,2-dinitroethyl ether. This was verified by acidification of a portion of the salt (using acetic acid-urea solution) and distillation to yield ethyl 2,2-dinitroethyl ether, b.p. 63-70° (2.5-2.7 mm.), n_D^{20} 1.4342, d_{20}^{20} 1.256; MR_D (calcd.) 33.76, MR_D (found) 34.04; lit. values,[4] b.p. 100° (11 mm.) Potassium ethyl 2,2-dinitroethyl ether gave the following analysis:

Calcd. for $C_4H_7N_2O_5K$: C, 23.76; H, 3.48; N, 13.86. Found: C, 24.04, 23.15[x]; H, 3.72, 3.69; N, 14.39, 14.20.

[x]The analyst reported that when potassium dichromate was added to these samples (to prevent formation of carbonates) violent explosions ensued upon combustion. The values for carbon, therefore, can only be considered approximate.

The yield of potassium ethyl 2,2-dinitroethyl ether was determined by comparing the ultraviolet spectrum of the purified salt with that of the crude salt. The purified salt showed E_{max} = 1.09, 1.10 at 365 mμ (C = 0.650 x 10^{-4} M); $k_{average}$ = 16820. The crude salt (C = 1.352 x 10^{-4}M) showed E_{max} = 1.58 at 365 mμ; k_{crude} = 11630. Thus, the crude salt contains 69.1% potassium ethyl 2,2-dinitroethyl ether (or 0.691 x 13.11 g. = 9.06 g.); this represents a yield of 89.6%.

5. REACTION OF PIPERIDINE WITH 1-BROMO-1,1-DINITROETHANE.

(a) Preparation of 1-bromo-1,1-dinitroethane: A modification of ter Meer's procedure[5] was employed. 1,1-Dinitroethane (12.05 g., 0.10 mole) stirred with water (50 ml.) at 0-5°, was allowed to react with an aqueous solution of sodium hydroxide (4.0 g. in 70 ml.). To the cold solution of sodium 1,1-dinitroethane was added during two hours a solution of bromine (16.00 g., 0.10 mole) in water (1200 ml.). The resulting reaction mixture was pale-yellow, and a small pool of colorless oil settled to the bottom. The organic matter was extracted with methylene chloride, the extracts dried with calcium chloride and the solvent removed under vacuum. The pale-yellow, lachrymatory oil remaining was <u>1-bromo-1,1-dinitroethane</u> (13.9 g., 70% yield); this was immediately used without further purification.

(b) <u>Reaction with piperidine:</u> Piperidine (13.0 g., 0.15 mole) in anhydrous ether (40 ml.) was stirred in an ice-water bath while 1-bromo-1,1-dinitroethane (13.9 g. of crude material, 0.070 mole) in absolute ether (40 ml.) was added dropwise (1 hour). A salt precipitated during the addition. This was filtered and 20.7 g. of crude, orange-yellow product was recovered. The ultraviolet spectrum of this crude material showed a maximum at 380 mμ and a minimum at 300 mμ. This is indicative of piperidinium 1,1-dinitroethane rather than of N-(2,2-dinitroethyl)-piperidine (maximum at 365 mμ), the other possible product. The weight of sample taken was 0.0369 g. (in 1 l. of 10^{-3} M sodium hydroxide); since E_{max} was observed as 1.60 and $k_{1,1\text{-DNE}}$ is known to be 16350 ± 150, the concentration of piperidinium 1,1-dinitroethane is given by

$$c = \frac{E_{max}}{16350 \cdot d} = \frac{1.60}{16350 \cdot 1.005} = 0.974 \times 10^{-4} \text{ mole/l.}$$

Therefore, the crude salt contains 54% piperidinium 1,1-dinitroethane (11.2 g., 78% of the theoretical amount). The crude salt (2.00 g.) was recrystallized, upon solution in methanol (6.0 ml.) at room temperature, by cooling at 0° for several hours. There were recovered 0.77 g. of orange crystals (parallelopipeds) melting at 106-109°; upon recrystallization the yellow crystals formed melted at 106-107°.

An authentic sample of piperidinium 1,1-dinitroethane was prepared by adding piperidine (1.10 g., 0.0128 mole) to 1,1-dinitroethane (1.54 g., 0.0128 mole) in methanol at room temperature. Some heat was evolved and the solution turned yellow; no solid precipitated, even at 0°, until absolute ether was added. The salt product separated as bright-yellow, minute crystals; the yield was 2.35 g. (89%), m.p. 114.5-115.5° (dec.). On admixture with the prepared sample of piperidinium 1,1-dinitroethane, a slight depression of melting point (104-106° (dec.)) was observed.

Both samples were again recrystallized. The prepared sample melted at 106.5-107.5°; the authentic sample melted at 114-115°; the mixture melted at 106-107°. The prepared sample was reacted with silver nitrate to prepare the silver salt. On analysis, the following result was observed:

<u>Anal.</u> Calcd. for silver 1,1-dinitroethane: Ag, 47.5%.
Found : Ag, 44.2%.

The conclusion drawn is that the recrystallized salt is somewhat impure piperidinium 1,1-dinitroethane.

6. THE REACTION OF SILVER 1,1-DINITROETHANE WITH METHYL IODIDE.

Silver 1,1-dinitroethane (45.8 g., 0.20 mole) dissolved in acetonitrile (250 ml., dried and distilled from phosphorus pentoxide) was stirred in an ice-water bath while methyl iodide (60 g., 0.43 mole) was slowly added (one hour). A pale yellow precipitate (silver iodide) was formed. Stirring at room temperature was continued for two hours. During this time, a sharp (formaldehyde) odor was detected from the reaction mixture. The silver iodide was filtered and washed thoroughly with ether. The filtrate was evaporated under vacuum. The residue was dissolved in ether and extracted with dilute sodium hydroxide (ca. 0.2 mole); the basic extract was immediately acidified by pouring into excess dilute sulfuric acid covered with a layer of ether.

The acid-free ether solution was dried with calcium chloride and evaporated under vacuum. The residue, comprised mainly of 2,2-dinitropropane, weighed 12.0 g. An attempt was made to purify the oily product by recrystallization from Skellysolve B. A gummy orange residue (0.7 g.) remained after dissolution of the bulk of the oil. On evaporation and freezing, crystals of 2,2-dinitropropane precipitated. On standing at room temperature (34-35°C.), however, the crystals melted and dissolved (some solvent still present; two layers (solvent and product) were present). Further purification, by means of steam distillation, yielded a colorless oil which, on standing in a refrigerator, crystallized to a waxy white solid. This product was practically pure 2,2-dinitropropane (3.65 g., 13.6% yield) m.p. 48-52°.

The acidic ether extract, after drying with calcium chloride, was also evaporated under vacuum. The yellow residual oil weighed 3.4 g. This was vacuum distilled to yield impure 1,1-dinitroethane, b.p. 58-61° (4.5 mm.), n_D^{20} 1.4376; the yield was 2.34 g. (9.8%). The physical constants for pure 1,1-dinitroethane are: b.p. 55-57° (4-5 mm.), n_D^{20} 1.4345. On standing at room temperature for several days, the distilled oil turned red in color and a minute quantity of white needles precipitated. These crystals melted at 128-145°; the composition of this material is unknown.

7. PREPARATION OF SODIUM AND LITHIUM TRIMETHOXYBOROHYDRIDES.

Methyl borate (104 g., 1 mole) was added to a stirred refluxing mixture of tetrahydrofuran (500 ml.) and the alkali hydride (NaH or LiH, 1 mole) at a rate such that the reflux could be controlled. The alkali hydride dissolved rapidly. Upon completion of the addition of methyl borate, the mixture was refluxed for ten minutes, cooled, and then allowed to settle. After the clear solution had been decanted, tetrahydrofuran (200 ml.) was added to the residue and the resulting mixture was centrifuged and decanted. The decantates were combined and the concentration of the alkali trimethoxyborohydride was determined titrimetrically (manometric) by the method of Krynitsky, Johnson, and Carhart, Anal. Chem., 20, 311 (1948). The yield of alkali trimethoxyborohydride ranges from 82-90%, depending on the purity of the alkali hydride used.

8. REDUCTION OF METHYL 4-METHYL-4-NITROPENTANOATE WITH SODIUM TRIMETHOXY-BOROHYDRIDE; 4-METHYL-4-NITRO-1-PENTANOL.

A mixture of methyl 4-methyl-4-nitropentanoate[15] (43 g., 0.25 mole) in tetrahydrofuran (100 ml.) was added to a 1.3 M solution (200 ml., 0.26 mole) of sodium trimethoxyborohydride in tetrahydrofuran. No reaction was apparent at room temperature. The mixture was then refluxed for eight hours, cooled, and hydrolyzed with hydrochloric acid (100 ml., 6 N). The resulting two layer system was distilled to remove solvents and to decompose any borate esters that were present. The residue was cooled and extracted with ethyl ether. The extract was dried over sodium sulfate and distilled to give 4-methyl-4-nitro-1-pentanol (32 g., 92% yield), b.p. 83-84° (0.3 mm.), $n_D^{19.5}$ 1.4506, lit.[15] 111-115° (3 mm.), $n_D^{19.4}$ 1.4507.

9. REDUCTION OF METHYL 4-NITROBUTANOATE WITH SODIUM TRIMETHOXYBOROHYDRIDE; 4-NITRO-1-BUTANOL.

By using the preceding procedure for preparing 4-methyl-4-nitro-1-pentanol from methyl 4-methyl-4-nitropentanoate, methyl 4-nitrobutanoate (22.6 g., 0.15 mole) was reduced with 1.3 M sodium trimethoxyborohydride solution (120 ml., 0.156 moles) to give 4-nitro-1-butanol (14.5 g., 80% yield), b.p. 74-75° (0.5 mm.), $n_D^{19.5}$ 1.4509, lit.[13] 103.0-103.5° (2 mm.), $n_D^{19.6}$ 1.4510.

10. REDUCTION OF 4-METHYL-4-NITROPENTANAL WITH SODIUM TRIMETHOXYBORO-HYDRIDE; 4-METHYL-4-NITRO-1-PENTANOL.

4-Methyl-4-nitropentanal (29 g., 0.2 mole) was added to a tetrahydrofuran solution of sodium trimethoxyborohydride (0.7 M, 200 ml.). A slight exothermic reaction occurred. After one hour the reaction mixture was decomposed with hydrochloric acid (6 N, 100 ml.) and extracted with ethyl ether. The ether extract was washed with aqueous sodium carbonate solution, dried with sodium sulfate, and distilled to give 4-methyl-4-nitro-1-pentanol (26 g., 90% yield), b.p. 82-83° (0.3 mm.).

11. REDUCTION OF 5,5-DINITRO-2-HEXANONE WITH SODIUM TRIMETHOXYBORO-HYDRIDE; 5,5-DINITRO-2-HEXANOL.

By using the previous procedure for reducing 4-methyl-4-nitropentanal to 4-methyl-4-nitro-1-pentanol, 5,5-dinitro-2-hexanone (19.0 g., 0.10 mole) was reduced to 5,5-dinitro-2-hexanol (17.0 g., 89% yield), b.p. 101-102° (0.5 mm.), $n_D^{19.5}$ 1.4631; lit.[15] 104.0-104.5° (0.6 mm.), $n_D^{20.0}$ 1.4636.

12. HYDROLYSIS OF METHYL 4-METHYL-4-NITROPENTANOATE; 4-METHYL-4-NITRO-PENTANOIC ACID.

A mixture of methyl 4-methyl-4-nitropentanoate (35 g. 0.2 mole) and hydrochloric acid (100 ml., 12 N) was refluxed for one hour; the mixture became homogeneous. Water (50 ml.) was added and the mixture was cooled. The resulting solution was extracted with ethyl ether, dried with sodium sulfate, evaporated, and then distilled under reduced pressure, to yield, after removal of an unidentified forerun, 4-methyl-4-nitropentanoic acid (27 g., 84.5% yield), b.p. 130° (1.0 mm.), 124° (0.6 mm.), $n_D^{19.5}$ 1.4515, neut. equiv. calc. 161, neut. equiv. found 159, 160.

13. REDUCTION OF p-NITROBENZOYL CHLORIDE, p-NITROBENZALDEHYDE.

Sodium trimethoxyborohydride (14 g., 1.094 moles) in tetrahydrofuran (100 ml.) was added (15 min.) to a mixture of p-nitrobenzoyl chloride (19.0 g., 0.1 mole) in tetrahydrofuran at -25°. After the addition was completed, the mixture was kept at -25° for 10 minutes and then allowed to warm to room temperature. The mixture was poured, with stirring, into water (700 ml.), and a yellow oil separated which then solidified. The solid was filtered and recrystallized from ethanol-water to give crude p-nitrobenzaldehyde (14.5 g.), m.p. 96-97°. Further recrystallization of the product from toluene-ligroin (1:4) gave p-nitrobenzaldehyde (11 g.) in 74% yield, yellow-white crystals, m.p. 103-104°, lit.[26] 106°.

14. PREPARATION OF 4-METHYL-4-NITROPENTANOYL CHLORIDE.

4-Methyl-4-nitropentanoic acid (18.96 g., 0.118 mole) was added to a mixture of thionyl chloride (20 ml.) and pyridine (one drop). Gases were evolved immediately; after the rapid reaction had subsided, the mixture was refluxed on a steam bath for a few minutes. Subsequent distillation of the mixture, after removal of the excess thionyl chloride, yielded 4-methyl-4-nitropentanoyl chloride (19.5 g., 0.115 moles, 98% yield) as a colorless fuming oil, b.p. 95° (6 mm.), 86-7° (2 mm.).

15. REDUCTION OF 4-METHYL-4-NITROPENTANOYL CHLORIDE; 4-METHYL-4-NITROPENTANAL.

A solution of sodium trimethoxyborohydride (15.5 g., 0.121 moles) in tetrahydrofuran (150 ml.) was added dropwise in 30 minutes to 4-methyl-4-nitropentanoyl chloride (19.5 g., 0.115 mole) in tetrahydrofuran (150 ml.). The temperature was maintained from -40° to -30° for 20 minutes, and the mixture was then allowed to warm to room temperature. After hydrochloric acid (100 ml., 3 N) had been added, the mixture was extracted with ethyl ether. The ether extract was washed with saturated sodium carbonate solution and dried with sodium sulfate. An aliquot of the ether solution on treatment with 2,4-dinitrophenylhydrazone-phosphoric acid solution, gave a hydrazone, which after recrystallization from ethanol, melted at 133°, lit.[13] 130.5-131.0°. Evaporation and distillation of the mixture gave 4-methyl-4-nitropentanal (10.9 g., 66% yield), b.p. 88-89° (3 mm.), $n_D^{19.5}$ 1.4467, lit.[13] 1.4469. The higher boiling fractions, presumably 4-methyl-4-nitro-1-pentanol and unreduced ester, were not identified.

16. PREPARATION OF 4,4-DINITROPENTANOYL CHLORIDE.

By using the procedure for preparation of 4-methyl-4-nitropentanoyl chloride, 4,4-dinitropentanoic acid (20.65 g., 0.108 mole) was converted by thionyl chloride to 4,4-dinitropentanoyl chloride (19.8 g., 88% yield), b.p. 105-106° (1 mm.).

17. REDUCTION OF 4,4-DINITROPENTANOYL CHLORIDE; 4,4-DINITROPENTANAL.

A solution of sodium trimethoxyborohydride (10 g., 0.0782 mole) in tetrahydrofuran (100 ml.) was added dropwise to a mixture of 4,4-dinitropentanoyl chloride (15.7 g., 0.075 mole) and tetrahydrofuran (175 ml.) at -40°. The mixture was maintained at 140 to -30° for 20 minutes and then allowed to warm to room temperature. The mixture was hydrolyzed with hydrochloric acid (100 ml., 3N) and then extracted with ethyl ether. The ether extract was washed with sodium carbonate solution, dried with sodium sulfate, evaporated, and then distilled at reduced pressure to give 4,4-dinitropentanal (9.5 g., 72% yield), b.p. 100-101° (1 mm.), $n_D^{19.5}$ 1.4649, lit.[27] b.p. 97-97.5° (0.8 mm.), n_D^{20} 1.4650.

18. HYDROLYSIS OF METHYL 4-NITROPENTANOATE; 4-NITROPENTANOIC ACID.

Methyl 4-nitropentanoate (16.1 g., 0.1 mole) was added with stirring to a cooled solution of sodium hydroxide (9 g., 0.225 mole) in methanol (50 ml.) and water (50 ml.). After one hour, the solution was acidified with a mixture of phosphoric acid and urea, diluted with water to a volume of 150 ml., and then evaporated to a volume of 75 ml. to remove methanol. The residual solution was saturated with sodium chloride and extracted with ethyl ether. The ether extract was dried over sodium sulfate, evaporated, and then distilled at reduced pressure to give, after removal of the forerun (3 g., b.p. 55-95° (0.6 mm.)), 4-nitropentanoic acid, (7 g., 47.5% yield), b.p. 97-98° (0.6 mm.), $n_D^{19.5}$ 1.4417; neut. equiv. calc. 147, neut. equiv. found 145, 144.

19. PREPARATION OF 4-NITROPENTANOYL CHLORIDE FROM 4-NITROPENTANOIC ACID.

Distillation of a reaction mixture of 4-nitropentanoic acid (6.5 g., 0.044 mole), phosphorus trichloride (10 ml.), and benzene (50 ml.) gave 4-nitropentanoyl chloride (6.0 g., 83% yield) as a colorless liquid, b.p. 74-75° (2.0 mm.).

20. REDUCTION OF 4-NITROPENTANOYL CHLORIDE; 4-NITROPENTANAL.

4-Nitropentanoyl chloride (6.0 g., 0.036 mole), upon reduction with sodium trimethoxyborohydride(5.11 g., 0.04 mole) in the manner previously described for the preparation of 4-methyl-4-nitropentanal and 4,4-dinitropentanal, gave 4-nitropentanal (3.0 g., 63% yield) as a colorless oil, b.p. 79° (3 mm.), $n_D^{19.5}$ 1.4454; lit.[13] 79-81° (3 mm.), $n_D^{19.6}$ 1.4455. Reaction of 4-nitropentanal with 2,4-dinitrophenylhydrazone gave the hydrazone as yellow-orange crystals, m.p. 94-95° from ethanol; lit.[13] 96.0-96.5°.

21. HYDROLYSIS OF METHYL 4-NITROBUTANOATE; 4-NITROBUTANOIC ACID.

Upon following the procedure for preparation of 4-nitropentanoic acid from methyl 4-nitropentanoate, methyl 4-nitrobutanoate was hydrolyzed to 4-nitrobutanoic acid (4 g.), a colorless liquid in 26% yield, b.p. 91-92° (0.6 mm.). Analysis of this reaction product is in progress.

22. REDUCTION OF 2-METHYL-1-NITROPROPENE WITH SODIUM TRIMETHOXYBOROHYDRIDE; 2-METHYL-1-NITROPROPANE.

Procedure 1. A solution of 2-methyl-1-nitropropene (15.2 g., 0.15 mole) in ethyl ether (25 ml.) was added dropwise in 85 minutes to a stirred suspension of sodium trimethoxyborohydride (21.1 g., 0.15 mole plus 10% excess) in ethyl ether (125 ml.) and tetrahydrofuran (50 ml.) contained in a 300 ml., three-necked flask equipped with a stirrer, a dropping funnel, a thermometer and a drying tube. During addition the reaction mixture was kept at -2 to -5°; after addition was completed the mixture was stirred for 35 minutes at 0°. The mixture was then acidified in one hour at 0° with urea-acetic acid solution (60 g.). The mixture was transferred to a separatory funnel and saturated with sodium chloride; the aqueous layer was separated and extracted with ether (100 ml). The combined ether extract was washed with saturated sodium bicarbonate solution (2 x 150 ml.), saturated sodium bisulfite solution (2 x 150 ml.) and saturated sodium chloride solution (200 ml.). After drying the ether layer over anhydrous sodium sulfate and removal of the solvent on a steam bath, distillation of the product gave: (a) crude 2-methyl-1-nitropropane (9.94 g., 0.0964 mole, 64.3%) as a light yellow oil, b.p. 55-78° (70 mm.), n_D^{20} 1.4110-1.4187; (b) crude 2-methyl-1-nitropropene (1.83 g.), b.p. 67-71° (25 mm.), n_D^{20} 1.4509-1.4619; (c) a brown residue (0.5 g.).*

The crude 2-methyl-1-nitropropane was dissolved in ether (150 ml.) and washed with saturated sodium bisulfite solution (3 x 150 ml., 5 minutes with each portion) to remove contaminating nitroolefin. Distillation of the product, after drying the ether solution and removing the ether on a steam bath, gave pure 2-methyl-1-nitropropane in slightly lower yield, b.p. 69-70.7° (70 mm.), n_D^{20} 1.4090, d_{20}^{20} 0.9627; MR_D (calcd.) 26.33, MR_D(found) 26.46; lit.[2] b.p. 66.9-67.5° (60 mm.), n_D^{20} 1.4084, d_4^{20} 0.965; lit.[28] b.p. 140.5°, d_{25}^{25} 0.9625, n_D^{25} 1.4050.

The structure of 2-methyl-1-nitropropane was proven by its conversion to 2-methyl-1-propanal via the Nef reaction followed by preparation of 2-methyl-1-propanal 2,4-dinitrophenylhydrazone, m.p. 179-181°. The melting point of the derivative was not depressed when mixed with an authentic sample, m.p. 179-181°.

An infrared spectrum of the 2-methyl-1-nitropropane (sandwich cell) contained a strong band for the mononitro (6.4 microns) group and no bands for a carbonyl group (5.7 microns), a mononitro group attached to an unsaturated carbon atom (6.5 microns) or a carbon-carbon double bond (6.0 microns).

Procedure 2. The experiment was conducted as above except after addition of the 2-methyl-1-nitropropene was completed the mixture was stirred for 30 minutes at 34°. Distillation of the product gave: (a) crude 2-methyl-1-nitropropane (7.35 g., 0.0713 mole, 47.5%), b.p. 55-78° (70 mm.), n_D^{20} 1.4130-1.4196; (b) crude 2-methyl-1-nitropropene (3.82 g.), b.p. 62-68° (25 mm.), n_D^{20} 1.4369-1.4610; (c) unidentified high boiling material* (0.89 g.), b.p. 86-90° (0.6 mm.), n_D^{20} 1.4683; (d) residue (1.2 g.).*

* Possibly formed by Michael condensations of the 2-methyl-1-nitropropene and 2-methyl-1-nitropropane.

Procedure 3. The experiment was conducted according to procedure 1, except, after addition of the 2-methyl-1-nitropropene was completed, the mixture was stirred for 18 hours at + 2°. Distillation of the product gave: (a) crude 2-methyl-1-nitropropane (9.08 g., 0.0881 mole, 58.7%), b.p. 55-76.5° (70 mm.), n_{20}^{20} 1.4129-1.4192; (b) crude 2-methyl-1-nitropropene (2.79 g.), b.p. 60-71° (24 mm.), n_D^{20} 1.4355-1.4622; (c) unidentified high boiling material* (1.21 g.), b.p. 80-90° (0.6 mm.), n_D^{20} 1.4637; (d) residue (0.5 g.).

Fraction (c) was redistilled 3 times to give a colorless liquid which turned yellow in a few hours, b.p. 90° (0.6 mm.), n_D^{20} 1.4683. Further identification of this product is in progress.

Anal. (Found) C, 56.20, 56.08; H, 8.38, 8.51; N, 11.82, 11.71

23. REDUCTION OF 2-METHYL-1-NITROPROPENE WITH LITHIUM BOROHYDRIDE; 2-METHYL-1-NITROPROPANE.

A solution of lithium borohydride (3.1 g., 0.0125 mole plus 10% excess) in tetrahydrofuran (15 ml.) and ethyl ether (30 ml.) was added in small portions to 2-methyl-1-nitropropene (5.05 g., 0.05 mole) in ethyl ether (10 ml.) contained in a 150 ml., round-bottomed flask equipped with a reflux condenser. After the initial reaction had subsided, the reaction mixture was allowed to stand at room temperature for 3 hours and then refluxed for one hour. The mixture was cooled to 0° and acidified in 60 minutes with urea-acetic acid solution[29] (25 ml.); the temperature of the mixture was maintained at -3 to -5°. The mixture was transferred to a separatory funnel and ethyl ether (100 ml.) and saturated sodium bicarbonate (100 ml.) were added. After shaking the mixture vigorously, the mixture was saturated with sodium chloride; the aqueous phase was separated and extracted with ethyl ether (100 ml.). The combined ether extract was dried over anhydrous sodium sulfate, evaporated on a steam bath, and then distilled to give: (a) crude 2-methyl-1-nitropropane (2.5 g., 0.0242 mole, 48.4% theory), b.p. 45-73°, n_D^{20} 1.4137-1.4212, d_{20}^{20} 0.9666; MR_D(calcd.) 26.33, MR_D (found) 26.61; (b) unidentified material (1.08 g.), b.p. 68-89° (7-9 mm.), n_D^{20} 1.4402-1.4517.

The infrared spectra of the crude 2-methyl-1-nitropropane contained a weak band for a carbon-carbon double bond (6.0 microns) and a weak band for a mononitro group attached to an unsaturated carbon atom (6.5 microns); thus the contaminant is probably 2-methyl-1-nitropropene. The infrared spectrum of high boiling product (b) contains only a band for the mononitro group (6.4 microns) and is probably a product resulting from the Michael condensation of 2-methyl-1-nitropropane and 2-methyl-1-nitropropene.

*Possibly formed by Michael condensations of the 2-methyl-1-nitropropene and 2-methyl-1-nitropropane

24. REACTION OF SODIUM TRIMETHOXYBOROHYDRIDE WITH 2-NITRO-1-BUTYL ACETATE.

A solution of 2-nitro-1-butyl acetate (16.1 g., 0.1 mole) in ethyl ether (25 ml.) was added dropwise in two hours to a stirred suspension of sodium trimethoxyborohydride (28.0 g., 0.2 mole plus 10% excess) in ethyl ether (125 ml.) and tetrahydrofuran (50 ml.) contained in a 300 ml., three-necked flask equipped with a stirrer, a dropping funnel, a thermometer and a drying tube. During addition the reaction mixture was kept at 3-4°; after addition was complete, the mixture was stirred for 18 hours at 3-4°. The reaction mixture was acidified in one hour at 0° with urea-acetic acid solution[29] (100 g.), transferred to a separatory funnel, and saturated with sodium chloride; the aqueous layer was separated and extracted with ethyl ether (100 ml.). The combined ether extract was washed with saturated sodium bicarbonate solution (2 x 150 ml.), saturated sodium chloride solution (200 ml.) and then dried over anhydrous sodium sulfate. Distillation of the product, after removal of solvent on a steam bath, gave the following fractions which are mixtures of 2-nitro-1-butanol and 2-nitro-1-butyl acetate:

Fraction	Boiling Range, °C.	Pressure	Weight	n_D^{20}	% 2-nitro-1-butanol
1	50-66.5	1 mm.	0.37 g.	1.4318	49
2	66.5-64	1-0.7	5.26	1.4339	52
3	64-65	0.7	2.86	1.4347	61
4	65	0.7	0.37	1.4357	71
Residue			0.5		

The infrared spectra of fraction 2 (sandwich cell) contained strong bands for the mononitro group (6.4 microns), the hydroxyl group (2.9 microns) and the carbonyl group (5.75 microns).

25. REACTION OF LITHIUM BOROHYDRIDE WITH 2-NITRO-1-BUTYL ACETATE.

A solution of 2-nitro-1-butyl acetate (16.1 g., 0.1 mole) in ethyl ether (25 ml.) was added dropwise in one hour to a stirred suspension of lithium borohydride (1.20 g., 0.05 mole plus 10% excess) in ethyl ether (125 ml.) and tetrahydrofuran (50 ml.) contained in a 300 ml., three-necked flask equipped with a stirrer, a thermometer, a drying tube and a dropping funnel. During addition the reaction mixture was kept at 4-5°; after addition was complete the mixture was stirred for 18 hours at 3-4°. The reaction mixture was acidified in one hour at 0° with urea-acetic solution (40 g.), transferred to a separatory funnel, and saturated with sodium chloride; the aqueous layer was separated and extracted with ether (100 ml.). The combined ether extract was washed with saturated sodium bicarbonate solution (2 x 150 ml.), saturated sodium chloride solution (200 ml.) and then dried over anhydrous sodium sulfate. Distillation of the product, after removal of solvent on a steam bath, gave the following fractions which are mixtures of 2-nitro-1-butanol and 2-nitrol-1-butyl acetate.

Fraction	Boiling Range	Pressure	Weight	n_D^{20}	% 2-Nitro-1-Butanol[x]
1	45-66°	1.3-1.0 mm.	0.10 g.	1.4308	19%
2	66-65.5	1.0-0.8	5.19	1.4359	73
3	65.5-65.0	0.8	4.65	1.4370	85
4	65	0.8	0.53	1.4382	98

An infrared spectrum of fraction 2 (sandwich cell) contained strong bands for the mononitro group (6.4 microns), the carbonyl group (5.7 microns) and the hydroxyl group (2.9 microns).

26. PREPARATION OF 3-METHYL-1-NITROBUTANE.

Silver nitrite (55 g., 0.35 mole, freshly recrystallized from hot water) was introduced into a 500 ml. round-bottomed three-necked flask fitted with a condenser, a stirrer and a dropping funnel. The flask was cooled to 0° and isoamyl bromide (50 g., 0.35 mole, b.p. 119-121°, n_D^{25} 1.4409, d_4^{20} 1.2202; prepared in 80% yield from reaction of phosphorus tribromide (1.2 mole) and isoamyl alcohol (2.0 moles, b.p. 129°, n_D^{25} 1.4064, d_4^{20} 0.8157 at -8 to 0°) was added dropwise in a course of 2 hours with continuous stirring. Stirring at 0° was continued for an additional 4 hours. The mixture was then slowly brought to room temperature and left overnight. Then the mixture was heated on a steam-bath for 4 hours. Ethyl ether (70 ml.) was added and the mixture refluxed for an additional 2 hours. The insoluble silver bromide was filtered and washed repeatedly with ether. The combined ether washings were distilled to give: Fraction 1, 1.7 g., b.p. 34-41°(12 mm.), n_D^{25} 1.4131; Fraction 2, 3.3 g., b.p. 41-48° (12 mm.), n_D^{25} 1.4141; Fraction 3, 4.8 g., b.p. 48-54° (12 mm.), n_D^{25} 1.4141; Fraction 4, 13.4 g., b.p. 54-58° (12 mm.), n_D^{25} 1.4157; d_4^{20} 0.965. Fraction 5, pot residue, 0.5 g. All fractions gave negative alcoholic-silver nitrate tests. Crude product, 23.8 g. (Fractions 1, 2, 3, 4 and 5), 61% yield.

Fraction 4 (13.4 g., b.p. 54-58° (12 mm.), n_D^{25} 1.4157, d_4^{20} 0.965) was rectified in a helix-packed column (1.5 x 13 cm.) to give: Fraction 4a, 2.2 g., b.p. 49-54° (12 mm.), n_D^{25} 1.4135; Fraction 4b, 10.1 g., b.p. 55-58° (12 mm.), n_D^{25} 1.4165, d_4^{20} 0.959.

To fractions 1, 2 and 3 (9.9 g. of impure product, cooled to 0°) was added 96% sulfuric acid (20 ml. precooled at 0°) at such a rate that the temperature did not rise about 5°. The solution was stirred for 5 minutes at 0° and then poured onto ice (100 g.) which was covered with petroleum ether (50 ml., b.p. 30-60°) The squeous layer was separated and extracted with fresh portions of petroleum ether. The ether extracts were combined, washed with water and dried over Drierite. The solvent was removed under reduced pressure. The crude product was

[x] Fractions were a mixture of 2-nitro-1-butanol and 2-nitro-1-butyl acetate.

distilled to give nitroisopentane (3.2 g.), b.p. 54-55° (11 mm.), n_D^{25} 1.4139, d_4^{20} 0.9564; lit.[30] b.p. 164°, n_D^{20} 1.41806, $d_4^{20.6}$ 0.9599.

To fractions 4a (2.2 g., b.p. 49-54° (12 mm.), n_D^{25} 1.4135, cooled to 0°) and 4b (10.1 g., b.p. 55-58° (12 mm.), n_D^{25} 1.4165, d_4^{20} 0.9592, cooled to 0°) was added 96% sulfuric acid (30 ml., precooled at 0°) at such a rate that the temperature did not rise above 5°. The solution was stirred for 5 minutes at 0° and then poured onto ice (150 g.) which was covered with 50 ml. of petroleum ether (b.p. 30-60°). The aqueous layer was separated and extracted with fresh portions of petroleum ether. The ether extracts were combined, washed with water and dried over Drierite. The solvent was removed under reduced pressure. The crude product was distilled to give pure 3-methyl-1-nitrobutane (7.5 g.) b.p. 54-54.5° (11 mm.), n_D^{25} 1.4149, d_4^{20} 0.9551; lit.[30] b.p. 164°, $n_D^{20.6}$ 1.41806, $d_4^{20.6}$ 0.9599.

27. **OXIDATIVE-NITRATION OF 3-METHYL-1-NITROBUTANE; 1,1-DINITRO-3-METHYLBUTANE.**

3-Methyl-1-nitrobutane (7.5 g., 0.064 mole, b.p. 54-54.5° (11 mm.), n_D^{25} 1.4149, d_4^{20} 0.9551) was dissolved in methanol (60 ml.) and added to aqueous sodium hydroxide (2.72 g., 97.9% assay in 30 ml. of water) at 5°. Sodium nitrite (4.77 g., 0.069 mole, 97% assay) was added and the cold solution was poured rapidly into a stirred mixture of aqueous silver nitrate (21.76 g., 0.13 mole), aqueous sodium hydroxide (5%, 1 drop), water (64 ml.) and ether (96 ml.) at 0-5°. After the precipitation of silver was complete, the cooling bath was removed and the mixture was allowed to stir for 0.5 hour. Saturated sodium chloride (5 ml.) was added and the mixture was filtered; the residue from the filtration was washed thoroughly with ethyl ether. The filtrate was separated and the aqueous layer was washed with ether. The ether extracts were combined, and, after benzene (20 ml.) had been added, were washed with saturated sodium chloride solution and water and dried over Drierite. The ether and benzene were distilled under reduced pressure. The crude dinitroisopentane was distilled under reduced pressure to give: Fraction 1, 1.65 g., b.p. 45°, (1.0 mm.), n_D^{25} 1.4358, d_4^{20} 1.1558; Fraction 2, 5.70 g., b.p. 45° (1.0 mm.), n_D^{25} 1.4360, d_4^{20} 1.1592. Total yield, 7.35 g., 61% theory. Fraction 2 was rectified in a helix-packed column (1.5 x 13 mm.) to give pure 1,1-dinitro-3-methylbutane, b.p. 42° (0.75 mm.), n_D^{20} 1.4380, n_D^{25} 1.4360, d_4^{20} 1.1590, MR_D (calcd.) 36.68, MR_D (found) 36.66.

Anal. for $C_5H_{11}N_2O_4$: Calcd. C, 37.03; H, 6.22; N, 17.28.
Found. C, 36.98, 37.15; H, 6.33, 6.16; N, 17.12, 17.20.

Potassium 1,1-dinitro-3-methylbutane (0.420 g., 87.1% theory) was obtained as a yellow salt by treating 1,1-dinitro-3-methylbutane (0.364 g., 0.0031 mole) in methanol (5 ml.) with methanolic potassium hydroxide (2 ml., 2.5 g.) and washing the filtered product several times with methanol (the yield of crude salt is lowered on washing with methanol); dec. range, 145-161°. The solubility of potassium 1,1-dinitro-3-methylbutane is: 1 part in 6.0 parts of water at 26°.

Silver 1,1-dinitro-3-methylbutane (0.364 g., 81.8% theory) was obtained as a water-insoluble yellow solid on mixing aqueous solutions of potassium 1,1-dinitro-3-methylbutane (0.308 g., 0.002 mole) and silver nitrate; dec. range, 145-155°, deposition of a silver mirror. Analysis of silver was performed by titrating silver 1,1-dinitro-3-methylbutane against standardized ammonium thiocyanate using 2 ml. of ferric ammonium sulfate indicator (prepared by dissolving 100 g. of salt in 100 ml. of 5 N nitric acid): (1) 0.1124 g. of silver 1,1-dinitro-3-methylbutane required 8.14 ml. of 0.05148 N ammonium thiocyanate; 40.2% Ag, (2) 0.0492 g. of silver 1,1-dinitro-3-methylbutane required 3.54 ml. of 0.05148 N ammonium thiocyanate; 40.0% Ag. Theory, 40.1% Ag.

28. OXIDATIVE NITRATION OF CYCLOHEXYLNITROMETHANE; CYCLOHEXYLDINITROMETHANE

(a) Preparation of Cyclohexyldinitromethane. Cyclohexylnitromethane (7.20 g., 0.050 mole, n_D^{20} 1.4635, d_4^{20} 1.0405, lit.[31] b.p. 98° (10 mm.), n_D^{20} 1.4688, d_4^{20} 1.0473, obtained from Dr. N. Kornblum) in methanol (75 ml.) was slowly mixed with aqueous sodium hydroxide (2.2 g., 0.55 mole, in 25 ml. water) and the solution was allowed to stand for 10 minutes below 15°. Sodium nitrite (3.8 g., 0.55 mole, 97% assay) was added and the mixture was cooled in an ice-bath and poured into a stirred solution of silver nitrate (17.0 g., 0.10 mole, in 50 ml. of water) and ether (50 ml.) at 5°. After 30 minutes the cooling bath was removed; brine (5 ml.) was added, and the mixture filtered by suction. The silver deposit was washed liberally with ether; the ether layer in the filtrate was separated, and the aqueous layer washed with ether. The ether washings were combined, washed with water, brine, and dried over Drierite. Distillation under reduced pressure (nitrogen atmosphere) gave crude cyclohexyldinitromethane (6.10 g., 64.9% yield), n_D^{25} 1.4730, b.p. 82-84° (1.0 mm.), d_4^{20} 1.201.

The crude product (b.p. 82-84° (1.0 mm.), n_D^{25} 1.4730, d_4^{20} 1.201) was rectified in a helix-packed column (1.5 x 13 mm.) to give pure cyclohexyldinitromethane: b.p. 84° (1 mm.), n_D^{25} 1.4735, d_4^{20} 1.2017.

Anal. for $C_7H_{12}N_2O_4$: Calcd: C, 44.67; H, 6.43; N, 14.89.
Found: C, 44.87, 44.93; H, 6.69, 6.45; N, 14.82, 14.98.

(b) Purification of Cyclohexyldinitromethane. Potassium cyclohexyldinitromethane was prepared by treating cyclohexyldinitromethane in methanol with methanolic potassium hydroxide. This crude potassium cyclohexyldinitromethane was recrystallized three times from hot water; dec. range 230-260°.

Potassium cyclohexyldinitromethane (8.03 g., 0.035 mole) was placed in a 500 ml. flask, fitted with a stirrer, a thermometer and a condenser. The potassium salt was dissolved in 300 ml. of water and cooled to 0°. With stirring, a solution (pre-cooled to 0°) of urea (5.1 g., 0.084 mole) dissolved in 20% aqueous acetic acid (3.0 g., 0.10 mole acid) was added (by means of a medicine dropper) over a period of 20 minutes. The two phase system thus produced was extracted with petroleum ether (3 x 50 ml.) and the extracts combined, dried over Drierite and distilled under reduced pressure in an atmosphere of nitrogen to give cyclohexyldinitromethane: 5.4 g., b.p. 80° (0.7 mm.), n_D^{20} 1.4765, d_4^{20} 1.2112, MR_D(calcd). 43.86, MR_D (found) 44.79.

Potassium cyclohexyldinitromethane (1.12 g., 93.3% of theory) was obtained as a yellow salt by treating cyclohexyldinitromethane (0.76 g., 0.0053 mole) in methanol (3 ml.) with methanolic potassium hydroxide (2 ml., 2.9 g.) and washing the filtered product several with methanol; recrystallization from hot water; dec. range, 230-260°. The solubility of potassium cyclohexyldinitromethane is 1 part in 34.3 parts of water at 24°.

Silver cyclohexyldinitromethane (0.616 g., 95.1% theory) was obtained as a water-insoluble yellow solid on mixing aqueous solutions of potassium cyclohexyldinitromethane (0.497 g.)and silver nitrate; dec. range 112-120°, initial deposition of a silver mirror. The following analyses of silver cyclohexyldinitromethane were obtained: (1) 0.0814 g. of silver cyclohexyldinitromethane required 5.32 ml. of 0.05148 N ammonium thiocyanate; Ag 36.3%, (2) 0.0917 g. of silver cyclohexyldinitromethane required 5.98 ml. of 0.05148 N ammonium thiocyanate; Ag 36.2%. Theory, Ag 36.6%.

29. PREPARATION OF 1-NITROPENTANE.

Silver nitrite (55 g., 0.35 mole, freshly recrystallized from hot water) was introduced into a 500 ml. round-bottomed three-necked flask fitted with a condenser, a stirrer and dropping funnel. The flask was cooled at 0° and n-amy bromide (50 g., 0.35 mole, Columbia Organic Chemicals, n_D^{25} 1.4421, d_4^{20} 1.2164) was added dropwise in the course of 2 hours with stirring. Stirring at 0° was continued for an additional 4 hours. The mixture was then slowly brought to room temperature and left overnight. The mixture was then heated on a steam-bath for 4 hours. Ethyl ether (75 ml.) was added to the mixture and refluxed for an additional 2 hours. The insoluble silver bromide was filtered and washed repeatedly with ether. The combined ether washings were distilled to give: Fraction 1, 1.4 g., b.p. 40-52° (23 mm.), n_D^{25} 1.4040, Fraction 2, 3.1 g., b.p. 52-65° (23 mm.), n_D^{25} 1.4120, Fraction 3, 1.9 g., b.p. 65-70° (22 mm.), n_D^{25} 1.4120, Fraction 4, 22.8 g., b.p. 70-72° (22 mm.), n_D^{25} 1.4158, d_4^{20} 0.958.

To Fraction 4, cooled to 0°, was added 96% sulfuric acid (40 ml., precooled at 0°) at such a rate that the temperature did not rise above 5°. The solution was stirred for 15 minutes at 0° and then poured on ice (150 g.) which was covered with petroleum ether (75 ml., b.p. 30-60°). The ether extracts were combined, washed with water and dried over Drierite. The solvent was removed under reduced pressure. The crude product was distilled to give 1-nitropentane (16 g.), b.p. 69-70° (19 mm.), n_D^{20} 1.4176, n_D^{25} 1.4153, d_4^{20} 0.9561; lit.,[32] b.p. 172-3°, n_D^{20} 1.4218, d_4^{20} 0.9475.

30. OXIDATIVE NITRATION OF 1-NITROPENTANE; 1,1-DINITROPENTANE.

(a) Preparation of 1,1-Dinitropentane. 1-Nitropentane (10.0 g., 0.085 mole, b.p. 69-70° (19 mm.), n_D^{25} 1.4153, d_4^{20} 0.9561) was dissolved in methanol (60 ml.) and added to aqueous sodium hydroxide (3.6 g., 97.9% assay, in 25 ml. of water) at 5°. Sodium nitrite (6.2 g., 0.09 mole, 97% assay) was added and the cold solution was poured rapidly into a stirred mixture of aqueous silver nitrate (30.6 g., 0.18 mole), aqueous sodium hydroxide (5%, 1 drop), water (70 ml.) and ether (125 ml.) at 0-5°. After the precipitation of silver was complete, the cooling bath was removed and the mixture was allowed to stir for 0.5 hours. Saturated sodium chloride (5 ml.) was added and the mixture was suction filtered; the residue from the filtration was washed thoroughly with ethyl ether. The filtrate was separated and the aqueous layer was washed with ether. The ether extracts were combined and, after benzene (20 ml.) had been added, were washed with saturated sodium chloride and water and dried with Drierite. After ether had been removed, the crude product was distilled under reduced pressure to give crude 1,1-dinitropentane: Fraction 1, b.p. 62-64° (2 mm.), 1.6 g., n_D^{25} 1.4365, d_4^{20} 1.1563, Fraction 2, b.p. 64-65° (2 mm.), 8.7 g., n_D^{25} 1.4370, d_4^{20} 1.1584. Total yield (Fractions 1 and 2), 10.3 g., 74.7% theory.

Fraction 2 (8.78 g., b.p. 64-65°(2 mm.), n_D^{25} 1.4370, d_4^{20} 1.1584) was distilled under reduced pressure (in an atmosphere of nitrogen) to give pure 1,1-dinitropentane, b.p. 53.5-54.5°(0.8 mm.), n_D^{20} 1.4387, n_D^{25} 1.4370, d_4^{20} 1.1584.

Anal. for $C_5H_{10}N_2O_4$: Calcd. C, 37.03; H, 6.22; N, 17.28.
Found: C, 37.11, 37.13; H, 6.22, 6.08; N, 17.38, 17.25.

Potassium 1,1-dinitropentane (6.87 g., 98.0% theory) was obtained as a yellow salt by treating 1,1-dinitropentane (5.75 g., 0.035 mole, b.p. 53.5-54.5° (0.9 mm.), n_D^{25} 1.4370, n_D^{20} 1.4387, d_4^{20} 1.1584) in methanol (10 ml.) with methanolic potassium hydroxide (20 ml., 10.0 g.) and washing the filtered product several times with ethyl ether. The product was recrystallized from hot water to give potassium 1,1-dinitropentane (6.41 g., 91.4% theory); dec. range, 185-202°. The solubility of potassium 1,1-dinitropentane is 1 part in 36 parts of water at 25°.

Silver 1,1-dinitropentane (0.479 g., 91.4% theory) was obtained as a water-insoluble yellow solid on mixing aqueous solutions of potassium 1,1-dinitropentane (0.390 g.) and silver nitrate; dec. range, 123-143°, deposition of a silver mirror. The following analyses of silver 1,1-dinitropentane were obtained: (1) 0.1276 g. of silver 1,1-dinitropentane required 9.15 ml. of 0.05148 N ammonium thiocyanate; % Ag 39.8%, (2) 0.1350 g. of silver 1,1-dinitropentane required 9.70 ml. of 0.05148 N ammonium thiocyanate; % Ag 39.9%. Theory, 40.1%.

(b) Purification of 1,1-Dinitropentane. Potassium dinitropentane (5.25 g., 0.026 mole, recrystallized twice from hot water) was placed in a one liter, three-necked flask equipped with a stirrer, a thermometer and a condenser. The potassium salt was dissolved in 400 ml. of water and cooled to 0°. With stirring, a solution of urea (5.1 g., 0.085 mole, precooled to 0°) which was dissolved in 30 g. of 20% aqueous acetic acid (0.10 mole acid) was added (by means of a medicine dropper) over a period of 20 minutes. The two phase system thus produced was extracted with petroleum ether (3 x 50 ml.) and the extracts were combined, dried over Drierite. After petroleum ether was distilled, the crude dinitropentane was distilled under reduced pressure (nitrogen atmosphere) to give: 3.55 g., b.p. 63.5° (2 mm.), n_D^{20} 1.4387, n_D^{25} 1.4368, d_4^{20} 1.1584, MR_D (calcd) 36.79, MR_D (found) 36.66.

31. PREPARATION OF 3,3-DIMETHYL-1-NITROBUTANE.

Silver nitrite (54 g., 0.35 mole, freshly recrystallized from hot water) was introduced into a 1 liter round-bottomed three-necked flask fitted with a condenser, a stirrer, and a dropping funnel. The flask was cooled to 0° and 1-bromo-3,3-dimethylbutane (58.4 g., 0.35 mole, prepared by reaction of t-butyl bromide, ethylene, and aluminum bromide at -30 to -5°, b.p. 54-55° (40 mm.), n_D^{25} 1.4420, d_4^{20} 1.1592; lit.,[19] b.p. 54° (40 mm.), n_D^{20} 1.4440, d_4^{20} 1.1556) was added dropwise in the course of 2 hours. Stirring at 0° was continued for an additional 4 hours. The mixture was brought to room temperature and left overnight while stirring. The mixture was then heated on a steam-bath for 6 hours. Ethyl ether (50 ml.) was added and the mixture was refluxed for an additional 2 hours. The insoluble silver bromide was filtered and washed repeatedly with ether. The combined ether washings were distilled to give: Fraction 1, 0.9 g., b.p. 45-60° (20 mm.), n_D^{25} 1.4209; Fraction 2, 11.9 g., b.p. 60-69° (20 mm), n_D^{25} 1.4212, d_4^{20} 0.9802, Fraction 3, 10.5 g., b.p. 69-70° (20 mm.), n_D^{25} 1.4212, d_4^{20} 0.9497.

Sulfuric acid (96%, 35 ml., precooled to 0°) was added to Fractions 2 and 3 (22.4 g., cooled to 0°) at a rate such that the temperature did not rise above 5°. The solution was then stirred for 15 minutes at 0° and then poured on ice (200 g.) which was covered with petroleum ether (75 ml., b.p. 30-60°). The aqueous layer was separated and extracted with fresh portions of petroleum ether. The ether extracts were combined, washed with water and dried over Drierite. The solvent was removed under reduced pressure and the residue was distilled under reduced pressure to give crude 1-nitro-3,3-dimethylbutane: Fraction 1, 3.74 g., b.p. 67-68° (20 mm.), n_D^{25} 1.4198, d_4^{20} 0.9551; Fraction 2, 6.71 g., b.p. 68-69° (20 mm.), n_D^{25} 1.4218, d_4^{20} 0.9467.

32. PREPARATION OF 3,3-DIMETHYL-1,1-DINITROBUTANE.

3,3-Dimethyl-1-nitrobutane (10.45 g., 0.80mole) was dissolved in methanol (100 ml.) and added to aqueous sodium hydroxide (3.6 g., 97.9% assay in 25 ml. of water) at 5°. Sodium nitrite (6.2 g., 0.09 mole, in 15 ml. of water) was added and the cold solution was poured rapidly into a stirred mixture of aqueous silver nitrate (30.6 g., 0.18 mole), aqueous sodium hydroxide (5%, 1 drop), water (70 ml.) and ether (125 ml.) at 0-5°. After the precipitation of silver was complete, the cooling bath was removed and the mixture was allowed to stir for 0.5 hours. Saturated sodium chloride (5 ml.) was added and the mixture was stirred for 0.5 hour. Saturated sodium chloride (5 ml.) was added and the mixture was filtered; the residue from the filtration was washed thoroughly with ethyl ether. The filtrate was separated and the aqueous layer was washed with ether. The ether washings were combined, washed with saturated sodium chloride solution, water and dried with Drierite. After ether was removed, the crude product was distilled under reduced pressure (nitrogen atmosphere) to give 3,3-dimethyl-1,1-dinitrobutane (6.10 g., 43.3% yield), b.p. 77° (5 mm.), n_D^{20} 1.4394, d_4^{20} 1.1190.

Potassium 3,3-dimethyl-1,1-dinitrobutane (1.66 g., 95.5% theory) was obtained as a yellow salt by treating 3,3-dimethyl-1,1-dinitrobutane (1.43 g., 0.0081 mole) in methanol (10 ml.) with methanolic potassium hydroxide and washing the filtered product several times with ethyl ether; dec. range, 260-273° after recrystallization from hot water. The solubility of potassium 3,3-dimethyl-1,1-dinitrobutane is 1 part in 15.3 parts of water at 32°.

Silver 3,3-dimethyl-1,1-dinitrobutane (0.271 g., 97.8% theory) was obtained as a water-insoluble orange solid on mixing aqueous solutions of potassium 3,3-dimethyl-1,1-dinitrobutane (0.268 g., 0.00098 mole) and silver nitrate; dec. range, 160-177°, deposition of a silver mirror.

Purification of 3,3-dimethyl-1,1-dinitrobutane. Potassium 3,3-dimethyl-1,1-dinitrobutane (4.27 g., 0.0201 mole, recrystallized twice from hot water) was placed in a 500 ml., round-bottomed, three-necked flask equipped with a stirrer, a thermometer and a condenser. The potassium salt was dissolved in water (250 ml.) and cooled to 0°. While stirring, a solution of urea (5.1 g., 0.085 mole, precooled to 0°) in 20% aqueous acetic acid (30 g., 0.10 mole acid) was added (by means of a medicine dropper) over a period of 20 minutes. The two phase system thus produced was extracted with petroleum ether (3 x 50 ml.) and the extracts were combined and dried over Drierite. After petroleum ether was distilled, the residue was distilled under reduced pressure to give pure 3,3-dimethyl-1,1-dinitrobutane: 2.75 g., b.p. 78-79° (5 mm.), n_D^{20} 1.4398, d_4^{20} 1.1185, MR_D (calcd,) 41.50, MR_D (found) 41.24. Analysis of the product is in progress.

33. PREPARATION OF 1,1-DINITROPROPANE.

1-Nitropropane (Commercial Solvents Corporation) was rectified in large quantities through an efficient column at constant boiling point (129.8° (atms. press.)); a final constant boiling fraction was taken and used for the preparation of pure 1,1-dinitropropane.

1,1-Dinitropropane was prepared in 80 per cent yield (10.32 g.) by oxidative-nitration of 1-nitropropane (8.9 g., 0.1 mole) and sodium nitrite (7.5 g., 97% assay) in sodium hydroxide (4.2 g., 97.9% assay, 1.05 mole in 45 ml.) with aqueous silver nitrate

(34.0 g., 0.2 mole in 100 ml.), aqueous sodium hydroxide (5%, one drop), and diethyl ether (150 ml.) at 0-5°. Distillation of the product gave colorless 1,1-dinitropropane (10.32 g., 80%), b.p. 52-54° (3 mm.), n_D^{20} 1.4331. Redistillation of the crude product gave pure 1,1-dinitropropane in the following fractions: (1) b.p. 56-59° (4 mm.), 1.45 g., n_D^{20} 1.4323; (2) 59.0-59.2° (4 mm.), 5.23 g., n_D^{20} 1.4335, and (3) 59.2-59.8° (4 mm.), 2.89 g., n_D^{20} 1.4333. Fraction 2 was used for titration, determination of neutralization equivalent, and for ultraviolet spectral analysis (max 1: mμ 383, log $\mathcal{E}$, 4.19; min: mμ 303, log $\mathcal{E}$ min. 2.86; max 2: mμ 227, log $\mathcal{E}_2$ 3.80).

34. REACTION OF 1-IODO-2-METHYLPROPANE AND SILVER NITRITE; 1-NITRO-2-METHYLPROPANE.

1-Iodo-2-methylpropane. Iodine (330 g., 1.3 moles) was added in one hour to a stirred mixture of red phosphorus (36.2 g., 1.17 moles) and isobutyl alcohol (120 g., 1.6 moles, b.p. 106.5-107.0° (atm.press.)) at 0°. The mixture was stirred at room temperature overnight and then refluxed for 20 minutes. The mixture was cooled; water (500 ml.) was added and the mixture was filtered. The organic layer was separated and washed successively with: cold water (3 times), cold conc. sulfuric acid, water (2 times), sodium thiosulfate solution, cold water, and saturated sodium chloride solution. The product was dried with Drierite and distilled to give 1-iodo-2-methylpropane: (1) 5.35 g., b.p. 114-116° (atm. press.), n_D^{25} 1.4931; (2) 123 g., b.p. 116-119° (atm. press.), n_D^{25} 1.4932; (3) 55.5 g., b.p. 92-93° (red. press.), n_D^{25} 1.4938. Yield 62%, calculated from isobutanol.

2-Methyl-1-nitropropane. 1-Iodo-2-methylpropane (Fraction 2, 46 g., 0.25 mole) was added slowly to stirred silver nitrate (46.2 g., 0.3 mole) at 0°. The mixture was allowed to warm to room temperature and was then stirred for 24 hours. The mixture was heated for two hours on a steam bath, then cooled, and ether was added. The ether solution was filtered, concentrated, and then distilled under nitrogen to give the following fractions: (1) 1.32 g., b.p. 26-36° (24 mm.), n_D^{25} 1.3995; (2) 6.45 g., b.p. 36-44° (24 mm.), n_D^{25} 1.4022, (3) 2.14 g., b.p. 40.5-42.0° (17 mm.), n_D^{25} 1.4041, (4) 8.02 g., b.p. 34.0-37.0° (11 mm.), n_D^{25} 1.4045, (5) 0.70 g., b.p. 40-60° (1 mm.), n_D^{25} 1.4421. Crude yield of 2-methyl-1-nitropropane, 70%.

Crude 2-methyl-1-nitropropane (Fractions 2, 3, and 4, 16.61 g., 0.161 moles) was cooled in an ice-salt mixture and then added to stirred cold conc. sulfuric acid cooled by ice-salt. The stirred solution was kept below 0° for 15 minutes and then poured into a mixture of ice and petroleum ether. After the mixture had been stirred thoroughly, the two layers were separated; the aqueous layer was extracted several times with petroleum ether. The extracts were combined, washed twice with water, dried over Drierite, and distilled to give 2-methyl-1-nitropropane: (1) 1.08 g., b.p. 51.0-52.5° (28 mm.), n_D^{25} 1.4072, and (2) 5.45 g., b.p. 52.0-52.5° (28 mm.), n_D^{25} 1.4072, d_{20}^{20} 0.964. The yield of pure 2-methyl-1-nitropropane is 25%, based on 1-iodo-2-methylpropane.

35. PREPARATION OF 1,1-DINITRO-2-METHYLPROPANE.[2]

1,1-Dinitro-2-methylpropane was prepared in 70% yield by oxidative-nitration of 2-methyl-1-nitropropane (5.2 g., 0.05 mole) and sodium nitrite (3.8 g., 0.055 mole, 97% assay) in sodium hydroxide solution (2.1 g., 97.9% assay, 23 ml. of water and 5 ml. of methanol) with aqueous silver nitrate (17 g., 0.10 mole, 50 ml. of water) and ethyl ether at 0°. Upon isolation of the reaction product in the usual manner, it was distilled under nitrogen to give the following fractions: (1) 1.31 g., b.p. 71-72° (6 mm.), n_D^{20} 1.4344; (2) 3.50 g., b.p. 72° (6 mm.), n_D^{20} 1.4352; (3) 0.25 g., b.p. 71-72° (6 mm.), n_D^{20} 1.4352.

Fraction 2 was redistilled under nitrogen to give pure 1,1-dinitro-2-methylpropane (2.93 g.), b.p. 54.4-55.0° (4 mm.), n_D^{20} 1.4353. This pure product was used for titration, ionization constant and ultra-violet studies (max 1: mμ 385, log ε, 4.03; min: mμ 303, log ε_{min} 2.90; max 2, mμ 231.5, log ε_2 3.86.

36. DECARBOXYLATION OF POTASSIUM ACID ACETYLENEDICARBOXYLATE; PROPIOLIC ACID.

Potassium acid acetylenedicarboxylate (622 g., 4.1 moles) was dissolved in the minimum amount of hot water. The mixture was heated for one hour on a water bath, refluxed for another hour, and then cooled. Ammonium sulfate (500 g.) was added and the mixture was made strongly acidic with sulfuric acid. The mixture was continuously extracted with diethyl ether, with rapid stirring, for several days. The ether extract was dried over calcium chloride, and after removal of the diethyl ether, was distilled under reduced pressure to give propiolic acid (91 g., 32% yield), b.p. 83-84° (50 mm.), n_D^{20} 1.4311; lit.[21] 1.4302.

37. PREPARATION OF METHYL PROPIOLATE.

Sulphuric acid (22.8 g., 0.23 mole) was added slowly with stirring to an ice cold solution of propiolic acid (76.0 g., 1.08 mole) in methanol (160 ml.). After standing at room temperature for two days (longer periods do not increase the yield), the mixture was poured into ice water and extracted with ether. The combined extracts were washed with sodium bicarbonate solution (10%) and dried over calcium chloride. After the ether was removed, the product (0.61 mole, 60% yield) was distilled at atmospheric pressure to give methyl propiolate (51.1 g., 0.61 mole, 60% yield), b.p. 101-102° (755 mm.), d_{20}^{20} 1.007, n_D^{20} 1.4073, MR_D^{20} (calc.) 20.32, MR_D^{20} (found) 20.56; lit.,[20] b.p. 102° (742 mm.), $n_D^{19.1}$ 1.4085, d (not reported).

38. PREPARATION OF METHYL 4-METHYL-4-NITRO-2-PENTENOATE.

Sodium methoxide solution (1.0 g. in 41 ml. of methanol) was added to a cold, stirred solution of methyl propiolate (10.0 g., 0.12 mole), 2-nitropropane (20.0 g., 0.22 mole), and methanol (20 ml.). The stirred solution was allowed to warm slowly to room temperature. After four hours, the mixture was poured into ice water, acidified with sulfuric acid, and extracted with ethyl ether. The combined extracts were dried over sodium sulfate and the ether was removed by vacuum distillation. The resultant residue was distilled under reduced pressure to give the following fractions: (1) 0.48 g., b.p. 90-96° (3.5 mm.), n_D^{20} 1.4680; (2) 0.63 g., b.p. 96-99° (3.5 mm.), n_D^{20} 1.4615; (3) 8.54 g., b.p. 99-100° (3.5 mm.), n_D^{20} 1.4621, d_{20}^{20} 1.1433; (4) 1.51 g., b.p. 100-101° (4.0 mm.), n_D^{20} 1.4621. The infra-red spectrum of fraction 3 indicated the presence of ester, conjugated double bond, and nitro groups (6.41 μ). The yield of methyl 4-methyl-4-nitro-2-pentenoate (fractions 2, 3 and 4) was 55.4%.

Anal. Calcd. for $C_7H_{11}NO_4$: C, 48.54; H, 6.40; N, 8.09.
Found: C, 48.60, 48.68; H, 6.64, 6.52; N, 8.02, 8.03.

39. BASE-CATALYZED REACTION OF 1,1-DINITROETHANE AND METHYL PROPIOLATE

Triton B (7 ml. of a 35% solution in methanol) was added slowly to a cold, well-stirred solution of methyl propiolate (5.0 g., 0.06 mole) and 1,1-dinitroethane (8.4 g, 0.07 mole) in methanol (20 ml.) (Premature removal of the reaction mixture may result in a fume-off). After having been stirred for six hours at room temperature, the mixture was poured into ice water and acidified with sulphuric acid. The mixture was extracted with ether several times; the combined ether extracts were then washed with sodium bicarbonate solution and dried over sodium sulphate.

After removal of the ether at reduced pressure, an attempt was made to vacuum distill (0.5 to 4 mm.) the residual oil. In every instance this resulted in a fume-off with copious evolution of oxides of nitrogen. The crude reaction product was then dissolved in ether and washed with sodium bicarbonate solution to remove acidic decomposition products. A second distillation resulted in considerable purification of the reaction product, presumably methyl 4,4-dinitro-3-pentanoate; however, decomposition of the volatile product was still extensive: (1) 1.1g., b.p. 87-97° (1.3-3.7 mm.), (2) 5.3 g., b.p. 97-100° (2.0-3.7 mm.), n_D^{20} 1.4728, and (3) 0.74 g., b.p. 100-101° (2 mm.), n_D^{20} 1.4735. Final identifications of fractions 2 and 3 are now in progress.

40. REACTION OF METHYL MAGNESIUM IODIDE AND 2-METHYL-1-NITROPROPENE; 2,2-DIMETHYL-1-NITROPROPANE AND 1,4-DINITRO-2,2,3,3-TETRAMETHYL-BUTANE.

2-Methyl-1-nitropropene (15.2 g., 0.15 mole) in ethyl ether (25 ml.) was added in 105 minutes at -65° to methyl magnesium iodide (33.3 g., 0.20 mole, 1.87 N in ether) and ethyl ether (250 ml.) in a one liter, three-necked flask equipped with a thermometer, a drying tube, a stirrer, and a dropping funnel. Formation of a complex occurred upon addition of each drop of 2-methyl-1-nitropropene. After addition was completed, the mixture was stirred for 1 hour at -70°, for 1.5 hours at -70 to -60° and for 1 hour at -60 to -15°. The mixture was then acidified below -10° with aqueous acetic acid (20 ml. of glacial acetic acid in 100 ml. of water); acidification required 30 minutes. The aqueous layer was separated and extracted with ether (100 ml.). The ether layers were combined and washed with saturated sodium bicarbonate solution (2 x 200 ml.), saturated sodium bisulfite solution (2 x 200 ml.) and saturated sodium chloride solution, and then dried over anhydrous sodium sulfate. The ether was evaporated from the mixture on a steam bath; a white solid (A) crystallized. The solid was filtered and washed with ethyl ether. The filtrate was distilled to give 2,2-dimethyl-1-nitropropane (6.13 g., 0.0524 mole, 34.9% theory) as a colorless liquid, b.p. 75-77° (63-64 mm.), n_D^{20} 1.4165. The residue from the distillation solidified and was recrystallized once from ethanol to give crude 2,2,3,3-tetramethyl-1,4-dinitrobutane (0.20 g., 0.00098 mole, 1.13%), m.p. 135-137°.

The initial precipitate (A) was recrystallized from hot ethanol as white crystals, m.p. 238-239°; the solid is insoluble in water and the usual organic solvents. Infrared data indicate the absence of nitro groups. Anal. (found) C, 51.91, 52.00; H, 7.66, 7.74; N, 14.52, 14.42. Identification of this product is now in progress.

41. REACTION OF 4-NITROBUTANOIC ACID WITH PHOSPHORUS TRICHLORIDE; 4-NITROBUTANOYL CHLORIDE.

Distillation of a reaction mixture of 4-nitrobutanoic acid (4 g., 0.03 mole) and phosphor trichloride (7 ml., 11 g., 0.08 mole) at reduced pressure gave 4-nitrobutanoyl chloride (3.9 g., 0.0258 mole) as a light yellow liquid in 86% yield; b.p. 69-70° (2 mm.). The 4-nitrobutanoyl chloride was used in the preparation of 4-nitrobutyraldehyde by selective-reduction with sodium trimethoxyborohydride.

42. REDUCTION OF 4-NITROBUTANOYL CHLORIDE; 4-NITROBUTANAL.

A mixture of sodium trimethoxyborohydride (3.2 g., 0.0251 mole) and tetrahydrofuran (30 ml.) was added dropwise to a solution of 4-nitrobutanoyl chloride (3.9 g., 0.0258mole) in tetrahydrofuran (30 ml.) at -40 . The temperature was maintained from -40 to -30° for 20 minutes, and the mixture was then allowed to warm to room temperature. After hydrochloric acid (25 ml., 3 N) had been added, the mixture was extracted with ethyl ether. The ether extract was washed with saturated sodium carbonate solution and then treated with excess 2,4-dinitrophenylhydrazine reagent. The reaction product was recrystallized from ethanol-water to give 4-nitrobutanal 2,4-dinitrophenylhydrazone (2.7 g., 0.0091 mole, two crops) in 36% yield, m.p. 135-136°; lit.[13] m.p. 136°.

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